10/804,747

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NEWS	1		Web Page URLs for STN Seminar Schedule - N. America
NEWS	2		"Ask CAS" for self-help around the clock
NEWS	3	FEB 28	PATDPAFULL - New display fields provide for legal status data from INPADOC
NEWS	4	FEB 28	BABS - Current-awareness alerts (SDIs) available
NEWS	5	MAR 02	GBFULL: New full-text patent database on STN
NEWS	6	MAR 03	REGISTRY/ZREGISTRY - Sequence annotations enhanced
NEWS	7	MAR 03	MEDLINE file segment of TOXCENTER reloaded
NEWS	8	MAR 22	KOREAPAT now updated monthly; patent information enhanced
NEWS	9	MAR 22	Original IDE display format returns to REGISTRY/ZREGISTRY
NEWS	10	MAR 22	PATDPASPC - New patent database available
NEWS	11	MAR 22	REGISTRY/ZREGISTRY enhanced with experimental property tags
NEWS	12	APR 04	EPFULL enhanced with additional patent information and new fields
NEWS	13	APR 04	EMBASE - Database reloaded and enhanced
NEWS	14	APR 18	New CAS Information Use Policies available online
NEWS	15	APR 25	Patent searching, including current-awareness alerts (SDIs), based on application date in CA/CAplus and USPATFULL/USPAT2 may be affected by a change in filing date for U.S. applications.
NEWS	16	APR 28	Improved searching of U.S. Patent Classifications for U.S. patent records in CA/CAplus
NEWS	17	MAY 23	GBFULL enhanced with patent drawing images
NEWS	18	MAY 23	REGISTRY has been enhanced with source information from CHEMCATS
NEWS	19	JUN 06	STN Patent Forums to be held in June 2005
NEWS	20	JUN 06	The Analysis Edition of STN Express with Discover! (Version 8.0 for Windows) now available
NEWS	21	JUN 13	RUSSIAPAT: New full-text patent database on STN
NEWS	22	JUN 13	FRFULL enhanced with patent drawing images

NEWS EXPRESS JUNE 13 CURRENT WINDOWS VERSION IS V8.0, CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP), AND CURRENT DISCOVER FILE IS DATED 13 JUNE 2005

NEWS HOURS	STN Operating Hours Plus Help Desk Availability
NEWS INTER	General Internet Information
NEWS LOGIN	Welcome Banner and News Items
NEWS PHONE	Direct Dial and Telecommunication Network Access to STN
NEWS WWW	CAS World Wide Web Site (general information)

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FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005

=> fil reg
COST IN U.S. DOLLARS

	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.21	0.21

FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005
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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 14 JUN 2005 HIGHEST RN 852282-01-0
DICTIONARY FILE UPDATES: 14 JUN 2005 HIGHEST RN 852282-01-0

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 18, 2005

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*                                                                    *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added,    *
* effective March 20, 2005. A new display format, IDERL, is now      *
* available and contains the CA role and document type information.  *
*                                                                    *
**********************************************************************
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Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=> s formaldehyde/cn
L1 1 FORMALDEHYDE/CN

=> d l1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2005 ACS on STN
RN 50-00-0 REGISTRY
ED Entered STN: 16 Nov 1984
CN **Formaldehyde (8CI, 9CI)** (CA INDEX NAME)
OTHER NAMES:
CN BFV
CN F-gen
CN Fannoform
CN Floguard 1015
CN FM 282
CN Fordor
CN Formalin
CN Formalith
CN Formic aldehyde
CN Formol
CN Fyde
CN Lysoform
CN Methaldehyde
CN Methanal
CN Methyl aldehyde
CN Methylene oxide
CN Morbicid
CN NSC 298885
CN Oxomethane
CN Oxymethylene
CN Paraform
CN Superlysoform
FS 3D CONCORD
DR 8005-38-7, 8006-07-3, 8013-13-6, 112068-71-0
MF C H2 O
CI COM
LC STN Files: ADISNEWS, AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN*, BIOBUSINESS, BIOSIS, BIOTECHNO, CA, CABA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CBNB, CEN, CHEMCATS, CHEMINFORMRX, CHEMLIST, CHEMSAFE, CIN, CSCHEM, CSNB, DDFU, DETHERM*, DIOGENES, DIPPR*, DRUGU, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2, GMELIN*, HODOC*, HSDB*, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MRCK*, MSDS-OHS, NAPRALERT, NIOSHTIC, PDLCOM*, PIRA, PROMT, PS, RTECS*, SPECINFO, TOXCENTER, TULSA, ULIDAT, USAN, USPAT2, USPATFULL, VETU, VTB
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

67660 REFERENCES IN FILE CA (1907 TO DATE)
6465 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
67727 REFERENCES IN FILE CAPLUS (1907 TO DATE)
19 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

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=> fil caplus
COST IN U.S. DOLLARS                                    SINCE FILE      TOTAL
                                                           ENTRY    SESSION
FULL ESTIMATED COST                                         6.87       7.08

FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005
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FILE COVERS 1907 - 15 Jun 2005  VOL 142 ISS 25
FILE LAST UPDATED: 14 Jun 2005  (20050614/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

  This file contains CAS Registry Numbers for easy and accurate
  substance identification.

=> s 50-00-0/rn
         67727 50-00-0
          6471 50-00-0D
L2       61794 50-00-0/RN
                (50-00-0 (NOTL) 50-00-0D )

=> s N-methyl?
       2806619 N
       1652749 METHYL?
        884815 ME
         10009 MES
        890941 ME
                (ME OR MES)
       2109049 METHYL?
                (METHYL? OR ME)
L3      166261 N-METHYL?
                (N(W)METHYL?)

=> s ?amine
L4     1415128 ?AMINE

=> s l2 and l3 and l4
L5         889 L2 AND L3 AND L4

=> s distill?
        112316 DISTILL?
        160014 DISTD
             1 DISTDS
        160014 DISTD
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                (DISTD OR DISTDS)
         24603 DISTG
        171283 DISTN
          1746 DISTNS
        172012 DISTN
                (DISTN OR DISTNS)
L6      362618 DISTILL?
                (DISTILL? OR DISTD OR DISTG OR DISTN)

=> s l5 and l6
L7          47 L5 AND L6

=> d l7 1-47 abs ibib
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L7 ANSWER 1 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Formaldehyde (FA), an occupational and environmental toxicant used extensively in the manufacturing of many household and personal use products, is known to induce squamous cell carcinomas in the nasal turbinates of rats and mice and squamous metaplasia in monkey noses. Tissue responses to FA include a dose dependent epithelial degeneration, respiratory cell hypertrophy, and squamous metaplasia. The primary target for FA-induced toxicity in both rodents and monkeys is the respiratory nasal epithelium. FA increases nasal epithelial cell proliferation and DNA-protein crosslinks (DPX) that are associated with subsequent nasal cancer development. To address the acute effects of FA exposure that might contribute to known pathol. changes, cDNA gene expression anal. was used. Two groups of male F344 rats received either 40 ul of distilled water or FA (400 mM) instilled into each nostril. Twenty-four hours following treatment, nasal epithelium was recovered from which total RNA was used to generate cDNA probes. Significance anal. of microarrays (SAM) hybridization data using Clontech Rat Atlas 1.2 arrays revealed that 24 of the 1185 genes queried were significantly up-regulated and 22 genes were significantly downregulated. Results for ten of the differentially expressed genes were confirmed by quant. real time RT PCR. The identified genes with FA-induced change in expression belong to the functional gene categories xenobiotic metabolism, cell cycle, apoptosis, and DNA repair. These data suggest that multiple pathways are dysregulated by FA exposure, including those involved in DNA synthesis/repair and regulation of cell proliferation. Differential gene expression profiles may provide clues that could be used to define mechanisms involved in FA-induced nasal cancer.

ACCESSION NUMBER: 2003:250610 CAPLUS
DOCUMENT NUMBER: 139:192642
TITLE: Formaldehyde-induced gene expression in F344 rat nasal respiratory epithelium
AUTHOR(S): Hester, Susan D.; Benavides, Gina B.; Yoon, Lawrence; Morgan, Kevin T.; Zou, Fei; Barry, William; Wolf, Douglas C.
CORPORATE SOURCE: US Environmental Protection Agency, Research Triangle Park, NC, USA
SOURCE: Toxicology (2003), 187(1), 13-24
CODEN: TXCYAC; ISSN: 0300-483X
PUBLISHER: Elsevier Science Ireland Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
REFERENCE COUNT: 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L7 ANSWER 2 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB A process for preparing trimethylol compds. (e.g., trimethylolpropane) and formic acid by the reaction of formaldehyde and aldehydes RCH2CHO [R = (un)substituted alkyl, (un)substituted cycloalkyl, (un)substituted aryl, (un)substituted aralkyl; e.g., butyraldehyde] in the presence of a nitrogen base (e.g., triethylamine) with distillation of the resulting reaction mixture in the presence of an auxiliary (e.g., N-methylpyrrolidone) is described. A process flow diagram is presented.

ACCESSION NUMBER: 2002:466749 CAPLUS
DOCUMENT NUMBER: 137:33975
TITLE: Process for preparing trimethylol compounds and formic acid from aldehydes and formaldehyde
INVENTOR(S): Dobert, Frank; Wagner, Paul; Klausener, Alexander; Eymann, Wolfgang; Feller, Rolf
PATENT ASSIGNEE(S): Germany
SOURCE: U.S. Pat. Appl. Publ., 8 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2002077502	A1	20020620	US 2001-17816	20011213
US 6441254	B2	20020827		
DE 10063937	A1	20020718	DE 2000-10063937	20001220
EP 1216979	A1	20020626	EP 2001-128486	20011207
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
JP 2002193854	A2	20020710	JP 2001-380156	20011213
CN 1359886	A	20020724	CN 2001-143351	20011220
PRIORITY APPLN. INFO.:			DE 2000-10063937 A	20001220
OTHER SOURCE(S):	MARPAT 137:33975			

L7 ANSWER 3 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Heteroat.-rich hydrocarbon oils (especially shale oils) are processed by solvent extraction with a polar solvent mixture containing a major amount of a polar solvent (with dipole moment >1 D), and a minor amount of water (as antisolvent), with, optionally, a minor amount of a C≤7-hydrocarbon (n-alkane, isoalkane, and cycloalkane), to yield a heteroatom-depleted raffinate and a heteroatom-rich extract The proportions of the polar solvent, water, and hydrocarbon are selected such that the coefficient of separation is >50%. Suitable polar solvents are selected from formaldehyde, formic acid, MeOH, acetaldehyde, HOAc, EtOH, propanol, isopropanol, furfural, phenol, sulfolane, N-methyl-2-pyrrolidone, and C≤10-carboxylic acids, aldehydes, ketones, ethers, esters, and amines. Addnl. refining options were described for further and sep. processing of both the raffinate and extract fractions (following distillation for removal of solvent, with appropriate recirculation back to the extraction step). The raffinate can be further processed to provide a high-quality synthetic crude petroleum for further refining. The heteroatom-rich extract can be used for the manufacture of a number of specialty chems., such as lubricant and fuel additives, biocides and pesticides, asphalt binders, solvents, diluting and solubilizing agents, etc.

ACCESSION NUMBER: 2000:842094 CAPLUS
DOCUMENT NUMBER: 134:31135
TITLE: Extraction with polar solvent-water antisolvent mixture for removal of heteroatomic compounds from shale oils
INVENTOR(S): Bunger, James W.; Cogswell, Donald E.
PATENT ASSIGNEE(S): James W. Bunger and Associates, Inc., USA
SOURCE: PCT Int. Appl., 69 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2000071494	A1	20001130	WO 2000-US14128	20000523
W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
EE 200100622	A	20030217	EE 2001-622	20000523
US 6875341	B1	20050405	US 2001-979702	20011126
PRIORITY APPLN. INFO.:			US 1999-135611P P	19990524
			WO 2000-US14128 W	20000523

REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L7 ANSWER 4 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB The oxazolidine derivs. (as corrosion inhibitors) are produced by condensation of N-methylethanolamine with aliphatic aldehydes in equi-mol. amts. in the presence of a neutral organic solvent. Preferably, the resulting products are purified by vacuum distillation Optionally, the products are dissolved in an oil base.

ACCESSION NUMBER: 1998:360777 CAPLUS
DOCUMENT NUMBER: 128:324754
TITLE: Volatile corrosion inhibitors for steels
INVENTOR(S): Marczak, Ryszard; Maciag, Artur; Prot, Tomasz; Wilczek, Maria
PATENT ASSIGNEE(S): Politechnika Radomska Im Kazimierza Pulaskiego, Pol.
SOURCE: Pol., 4 pp.
CODEN: POXXA7
DOCUMENT TYPE: Patent
LANGUAGE: Polish
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PL 173103	B1	19980130	PL 1994-301910	19940114
PRIORITY APPLN. INFO.:			PL 1994-301910	19940114

L7 ANSWER 5 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
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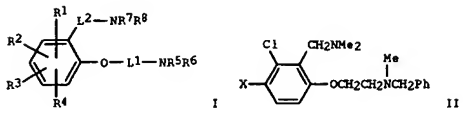

I II

AB The title compds. [I; R1 - R4 = H, halo, halo, halogenated alkyl, halogenated alkoxy, alkyl, alkoxy, cyano, a carbamoyl group of formula CONRaRb (wherein Ra, Rb = alkyl), alkoxy carbonyl group; or R1 and R2 together with the Ph ring represent an (un)substituted naphthalene ring; L1 = C2-6 alkylene optionally substituted by one or more C1-4 alkyl groups; R5 = H, alkyl; R6 = H, alkyl, (un)substituted phenylalkyl; or R5 and R6 together with the nitrogen atom to which they are attached represent a saturated 3-7 membered heterocyclic ring; L2 = C1-6 alkylene chain optionally substituted by one or more C1-4 alkyl groups; R7, R8 = H, alkyl; or R7 and R8 together with the nitrogen atom to which they are attached represent a saturated 3-7 membered heterocyclic ring] or pharmaceutically acceptable salts thereof which are antiinflammatory and/or antiallergic agents and/or immunomodulators and useful in treating rheumatic diseases and/or neurol. damage, are prepared Thus, 5.25 mL N-benzyl-N-**methylethanolamine**, 8.48 g Ph3P, and 5.09 mL di-Et azodicarboxylate were added to a solution of 6.0 g 3-chloro-2-(dimethylaminomethyl)phenol in THF and the resulting mixture was stirred at ambient temperature for 24 h to give, after vacuum **distillation** and treatment with ethereal HCl, a **benzylamine** derivative (II.2HCl; X = H). This compound and II.2HCl (X = Cl) in vitro inhibited the arachidonic acid release from zymosan-stimulated macrophages with IC50 of 15 and 8 μM, resp., and in vivo at 100 mg/kg p.o. inhibited 70% the carrageenan-induced paw edema in rats.

ACCESSION NUMBER: 1995:994305 CAPLUS
DOCUMENT NUMBER: 124:55553
TITLE: Preparation of 2-(aminoalkoxy)phenylalkylamines with antiinflammatory activity
INVENTOR(S): Rafferty, Paul; Tometzki, Gerald Bernard
PATENT ASSIGNEE(S): Boots Co. PLC, UK
SOURCE: PCT Int. Appl., 100 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9523127	A1	19950831	WO 1995-EP626	19950220
W: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US				
RW: KE, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
AU 9517586	A1	19950911	AU 1995-17586	19950220
EP 750607	A1	19970102	EP 1995-910506	19950220
EP 750607	B1	19990506		
R: DE, FR, GB, IT				
JP 09509422	T2	19970922	JP 1995-522119	19950220
ZA 9501420	A	19950825	ZA 1995-1420	19950221
US 5736568	A	19980407	US 1996-687584	19961125
PRIORITY APPLN. INFO.:			GB 1994-3639 A	19940225
			WO 1995-EP626 W	19950220
OTHER SOURCE(S):	MARPAT 124:55553			

L7 ANSWER 6 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB Disclosed is a one-step method for preparing N-alkylpiperazines which eliminates the initial preparation and isolation of piperazine which comprises reacting a carbonyl compound R''COR' where R" and R' = an alkyl group or H, and an **amine** H2NCH2CH2NHCH2CH2R''' where R''' is OH or NH2 in the presence of hydrogen over a metallic hydrogenation catalyst consisting essentially of nickel, copper and chromium. Thus, e.g., reaction of **aminoethylethanolamine** (208 g) with isobutyraldehyde (144 g) followed by hydrogenation/cyclization over nickel-copper-chromium catalyst afforded the iso-Bu derivative of **aminoethylethanolamine** as the main product; however, the ratio of isobutylpiperazine to piperazine was about 8:1. In comparison, the reaction of piperazine with isobutyraldehyde followed by hydrogenation over nickel-copper-chromium catalyst afforded a material that contained 21% piperazine and 30% N-isobutylpiperazine; separation of piperazine from the isobutylpiperazine was difficult (even though the isobutylpiperazine boiled at 182°) because piperazine deposited throughout the **distillation** train.

ACCESSION NUMBER: 1995:616516 CAPLUS
DOCUMENT NUMBER: 123:55921
TITLE: One-step preparation of N-alkylpiperazines which eliminates the initial preparation and isolation of piperazine
INVENTOR(S): Speranza, George P.; Templeton, James H.
PATENT ASSIGNEE(S): Huntsman Corporation, USA
SOURCE: U.S., 5 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5414087	A	19950509	US 1993-87093	19930707
PRIORITY APPLN. INFO.:			US 1993-87093	19930707
OTHER SOURCE(S):	CASREACT 123:55921; MARPAT 123:55921			

L7 ANSWER 7 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB In a process for production of an aromatic azomethine by reaction of an aniline with formaldehyde, formaldehyde is provided in the form of a product produced by contacting paraformaldehyde with from about 0.25 to about 3 mol equivalent of an aliphatic alc. having from 1 to 4 carbon atoms in the presence of a catalytic amount of a base. The azomethine may then be used to produce a haloacetanilide. Thus, e.g, one reactor was charged with 3.0 mol paraformaldehyde, 3.0 mol ethanol, 0.01 mol **triethylamine**, 1.0 mol xylene and 0.5 mol water, heated to 85-90° and agitated until the solution was clear; this solution was added to a reactor containing 1 mol of 2-methyl-6-ethylaniline and 2 mol of xylene at about 90°; the reaction was allowed to proceed with azeotropic **distillation** of water at atmospheric pressure at 95-126°; addition of chloroacetyl chloride afforded 96-97% of the N-chloromethyl-α-chloroacetanilide derivative

ACCESSION NUMBER: 1995:603984 CAPLUS
DOCUMENT NUMBER: 123:111656
TITLE: Process for producing aromatic azomethines by reaction of an aniline with formaldehyde provided in the form of a formaldehyde-alcohol complex
INVENTOR(S): Rodriguez, Gilbert
PATENT ASSIGNEE(S): Imperial Chemical Industries PLC, UK
SOURCE: U.S., 7 pp. Cont.-in-part of U.S. Ser. No. 680,468, abandoned.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5399759	A	19950321	US 1992-872775	19920422
HU 65592	A2	19940728	HU 1993-2620	19920320
HU 219568	B	20010528		
AT 154000	E	19970615	AT 1992-910655	19920320
ES 2102503	T3	19970801	ES 1992-910655	19920320
ZA 9202455	A	19930329	ZA 1992-2455	19920403
IL 101484	A1	19970415	IL 1992-101484	19920403
PRIORITY APPLN. INFO.:			US 1991-680468 B2	19910404
OTHER SOURCE(S):	CASREACT 123:111656; MARPAT 123:111656			

L7 ANSWER 8 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB The title polymers, useful in moldings, films, and fibers (no data), are prepared by the reaction of polymers containing the ethers CH2:C(X)CH2OCH2C(Y):CH2 (X, Y = CO2H, carboalkoxy, acyl, amido, or CN group) 1-99, (meth)acrylic acid or their (cyclo)alkyl esters 99-1, and comonomers 0-98% with primary amines of specified structure. Peroxy ester-initiated polymerization of 60 g di-Me 2,2'-(oxydimethylene)diacrylate (prepared from Me acrylate and paraformaldehyde in the presence of triethylenediamine) with 140 g MMA in THF at 65° gave 190 g copolymer, which was heated (10 g) with 10 g cyclohexylamine in N-methylpyrrolidone for 6 h with distillation of MeOH to give a polymer with N content 5.1% and glass temperature 235°.

ACCESSION NUMBER: 1994:192636 CAPLUS
DOCUMENT NUMBER: 120:192636
TITLE: Polymethacrylimides with high heat distortion resistance
INVENTOR(S): Besecke, Siegmund; Deckers, Andreas; Lauke, Harald
PATENT ASSIGNEE(S): BASF A.-G., Germany
SOURCE: Eur. Pat. Appl., 15 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 561230	A2	19930922	EP 1993-103460	19930304
EP 561230	A3	19931027		
EP 561230	B1	19960529		
R: BE, CH, DE, FR, GB, IT, LI, NL				
DE 4208994	A1	19930923	DE 1992-4208994	19920320
US 5338805	A	19940816	US 1993-31907	19930316
PRIORITY APPLN. INFO.:			DE 1992-4208994 A	19920320

L7 ANSWER 9 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

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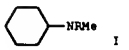

I

AB Title amines I (R = cyclohexyl, C1-6 linear or branched alkyl group) prepared by methylation with H2CO are purified by a distillation process involving: (i) preliminary distillation of MeOH, H2CO, and a portion of H2O; (ii) addition of 5-20-fold portion of C8-12 arylalkanes and/or cycloalkylalkanes (based on combined 5-15 mol% water content + HCO2H content (as formate salt)); (iii) continuous distillation of the resultant mixture (with inert gas bubbling and/or reduced pressure, as necessary) for 4-10 h with return of arylalkanes and/or cycloalkylalkanes to the distillation apparatus. Thus, the reaction mixture resulting from methylation of cyclohexylamine with H2CO was submitted to preliminary distillation for MeOH and partial H2O removal, resulting in the composition: I (R = Me) (90.2 mol%), other amines (0.4 mol%), H2O (8 mol%), HCO2H (1.4 mol%). To 1000 g of this mixture was added 800 g xylene mixture, and the resulting solution was distilled for 8 h with Ar bubbling (15 dm3) for 1 h; H2O and HCO2H were removed as a sep. phase, and the xylene mixture was returned to the distillation apparatus. I (R = Me) was obtained H2O- and HCO2H-free, in 99.7 mol% purity, by addnl. distn.

ACCESSION NUMBER: 1993:233533 CAPLUS
DOCUMENT NUMBER: 118:233533
TITLE: Process for purification of tertiary cyclohexylamines obtained by methylation with formaldehyde
INVENTOR(S): Palkovics, Istvan; Magi, Gabor, Mrs.; Torkos, Laszlo; Aranyi, Peter; Gemes, Istvan; Novotnik, Katalin
PATENT ASSIGNEE(S): Nitroil Vegyipari Termelo-Fejleszto Rt., Hung.
SOURCE: Hung. Teljes, 9 pp.
CODEN: HUXXBU
DOCUMENT TYPE: Patent
LANGUAGE: Hungarian
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
HU 61265	A2	19921228	HU 1991-439	19910211
HU 208667	B	19931228		
PRIORITY APPLN. INFO.:			HU 1991-439	19910211
OTHER SOURCE(S):	MARPAT 118:233533			

L7 ANSWER 10 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB The hazardous materials regulations under the Federal Hazardous Materials Transportation Act are revised based on the United Nations recommendations on the transport of dangerous goods. The regulations cover the classification of materials, packaging requirements, and package marking, labeling, and shipping documentation, as well as transportation modes and handling, and incident reporting. Performance-oriented stds. are adopted for packaging for bulk and nonbulk transportation, and SI units of measurement generally replace US customary units. Hazardous material descriptions and proper shipping names are tabulated together with hazard class, identification nos., packing group, label required, special provisions, packaging authorizations, quantity limitations, and vessel stowage requirements.

ACCESSION NUMBER: 1992:135528 CAPLUS
DOCUMENT NUMBER: 116:135528
TITLE: Performance-oriented packaging standards; changes to classification, hazard communication, packaging and handling requirements based on UN standards and agency initiative
CORPORATE SOURCE: United States Dept. of Transportation, Washington, DC, 20590-0001, USA
SOURCE: Federal Register (1990), 55(246), 52402-729, 21 Dec 1990
CODEN: FEREAC; ISSN: 0097-6326
DOCUMENT TYPE: Journal
LANGUAGE: English

L7 ANSWER 11 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB The continuous preparation of N,N-dimethylamines by the reaction of aldehydes with Me2NH and hydrogen under pressure at high temperature in the presence of Ni, Co, Cu, Mn, Fe, Rh, Pd and/or Pt-containing hydrogenation catalysts is claimed. After remaining starting material (Me2NH) and hydrogen are removed, 0.1-25% by weight HCHO or HCHO-forming substance are added and the mixture is distilled. This process permits nearly complete removal of secondary N-methylamines which are formed as by products. A reactor containing 300 mL catalyst RCH Ni52/35 (tablets; Ni catalyst on kieselguhr) was filled with Me2NBu and then charged with PrCHO (65 mL) and Me2NH (200 mL) at 105-110° and 8 MPa and hydrogen was charged at 34 L/h; remaining hydrogen and Me2NH were removed and during the subsequent distillation 37% aqueous HCHO (.apprx.3% with respect to Me2NBu) was fed into the crude product mixture at the bottom of the column. The distillate contained 99.65% by weight Me2NBu and 0.02% by weight MeNHBu. Omission of feed of aqueous HCHO gave a distillate containing 98.09% by weight Me2NBu and 1.22% by weight MeNHBu.

ACCESSION NUMBER: 1991:535511 CAPLUS
DOCUMENT NUMBER: 115:135511
TITLE: Process for the preparation of N,N-dimethylamines
INVENTOR(S): Kampmann, Detlef; Kniep, Claus; Lukas, Rainer
PATENT ASSIGNEE(S): Hoechst A.-G., Germany
SOURCE: Ger. Offen., 6 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 3942793	A1	19910627	DE 1989-3942793	19891223
EP 435072	A2	19910703	EP 1990-123912	19901212
EP 435072	A3	19920304		
EP 435072	B1	19940427		
R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE				
AT 104950	E	19940515	AT 1990-123912	19901212
ES 2055855	T3	19940901	ES 1990-123912	19901212
CA 2032362	AA	19910624	CA 1990-2032362	19901214
CA 2032362	C	20010327		
JP 06219993	A2	19940809	JP 1990-402867	19901217
JP 07072159	B4	19950802		
AU 9068373	A1	19910627	AU 1990-68373	19901221
AU 634007	B2	19930211		
PRIORITY APPLN. INFO.:			DE 1989-3942793 A	19891223
			EP 1990-123912 A	19901212

L7 ANSWER 12 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
GI

I

AB The title compds (I; A = C2-10 1,2- or 1,3-alkylene) were prepared by **N-methylation** of the parent cyclic urea using H2CO and excess HCO2H (the latter being removed by thermal decomposition in the presence of a tertiary **amine** and a Cu salt). Thus, a mixture of 1,3-propyleneurea 4 mol, HCO2H 20 mol, 50% aqueous H2CO 9-6 mol, Et3N 40 mol, and CuCl 40 mol was refluxed 16 h followed by **distillation** of volatiles;. Decomposition of HCO2H began at 150° and was complete after 4-6 h. Final **distillation** of the mixt at 23 mbar and 106-108° gave 80% I [A = (CH2)3].

ACCESSION NUMBER: 1990:440719 CAPLUS
DOCUMENT NUMBER: 113:40719
TITLE: Preparation of cyclic N,N'-dimethylureas by methylation with formic acid and formaldehyde
INVENTOR(S): Betz, Rainer; Hahn, Erwin; Fikentscher, Rolf
PATENT ASSIGNEE(S): BASF A.-G., Germany
SOURCE: Eur. Pat. Appl., 6 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 356973	A1	19900307	EP 1989-115871	19890829
EP 356973	B1	19921111		
R: DE, FR, GB, IT				
DE 3829848	A1	19900315	DE 1988-3829848	19880902
US 4970321	A	19901113	US 1989-397878	19890823
JP 02115171	A2	19900427	JP 1989-217641	19890825

PRIORITY APPLN. INFO.: DE 1988-3829848 A 19880902
OTHER SOURCE(S): CASREACT 113:40719; MARPAT 113:40719

L7 ANSWER 13 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB **N-Me** tertiary amines are prepared by continuous treatment of HCHO with nitriles in the presence of hydrogenation catalysts at 80-180° under 3-50 kg/cm2 gage H. Lauronitrile (I) was autoclaved with Raney Ni at 140° under 10 kg/cm2 gage H while adding an aqueous HCHO for 6 h and the reaction mixture was kept for 0.5 h, subsequently the reaction product was **distilled** to give 92.4% Me(CH2)11NMe2, vs. 70.0% for a control by a two-step reaction comprising (1) hydrogenation of I at 120° under 20 kg/cm2 gage H for 6 h and (2) purification of the resulting **laurylamine** and **N-methylation** under the same conditions.

ACCESSION NUMBER: 1989:406917 CAPLUS
DOCUMENT NUMBER: 111:6917
TITLE: Preparation of N-methyl tertiary amines from nitriles and formaldehyde
INVENTOR(S): Yokota, Yukinaga; Matsutani, Kazuto; Okabe, Kazuhiko
PATENT ASSIGNEE(S): Kao Corp., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63287752	A2	19881124	JP 1987-120949	19870518

PRIORITY APPLN. INFO.: JP 1987-120949 19870518

L7 ANSWER 14 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB Wastewaters from thiazone manufacturing are acidified to pH 0.3-0.5 with H2SO4 or HCl to hydrolyze **methylamine N-methyldithiocarbamate**; the CS2 formed is adsorbed on an activated C; HCHO is oxidized to HCOOH with air over a bed of pyrolusite; and the residual volatile organic compds. are removed by **distillation**

ACCESSION NUMBER: 1987:483309 CAPLUS
DOCUMENT NUMBER: 107:83309
TITLE: Treatment of wastewater from thiazone manufacture
AUTHOR(S): Marchenko, V. M.; Taran, P. N.
CORPORATE SOURCE: Inst. Kolloidn. Khim. Khim. Vody im. Dumanskogo, Kiev, USSR
SOURCE: Khimiya i Tekhnologiya Vody (1987), 9(3), 250-2
CODEN: KTVODL; ISSN: 0204-3556
DOCUMENT TYPE: Journal
LANGUAGE: Russian
OTHER SOURCE(S): CASREACT 107:83309

L7 ANSWER 15 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB A simple, rapid a.c. polarographic method for the determination of free and bound HCHO [50-00-0] in 0.1 N LiOH can be used to optimize methods for the production of HCH products, to follow the etherification of **N-methylol** compds. with alcs., and to analyze textiles finished with formaldehyde products. Free HCHO is determined at pH ≤9.2 since no dissociation of methylol groups occurs in this region; NCH2OH, NCH2OCH2OH, and OCH2OH are hydrolyzed in LiOH which also serves as the base electrolyte; NCH2OMe, NCH2OCH2N, and NCH2OCH2OMe were hydrolyzed by strong acids, the HCHO when free is **distilled**, and the **distillate** is analyzed polarog. When the substance to be analyzed produces interfering waves, as is the case with **hexamethylolmelamine** (I) [3089-11-0], the mercurimetric cyanide method is used to determine free HCHO.
Polarograms are given for I, N,N'-dimethylol-1,3-propyleneurea [3270-74-4], (MeO)2P(O)CH2CH2CONHCH2OH [20120-33-6], and Movin DC [53200-17-2].

ACCESSION NUMBER: 1975:580860 CAPLUS
DOCUMENT NUMBER: 83:180860
TITLE: Determination of free and bound formaldehyde in textile auxiliary agents by alternating current polarography
AUTHOR(S): Linhart, Karl
CORPORATE SOURCE: Leverkusen, Fed. Rep. Ger.
SOURCE: Melliand Textilberichte International (1975), 56(3), 240-5
CODEN: MTXIAW; ISSN: 0375-9350
DOCUMENT TYPE: Journal
LANGUAGE: German

L7 ANSWER 16 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Carbamoyloxyalkyl esters of sulfoalkyl, carbamylalkyl, cyanoalkyl, or phosphonoalkyl phosphonates or phosphonites are fire retardants for textiles. Thus, addition over 30 min of 849 g ethylene carbonate [96-49-1] to 722 g 25%NH3 at 20-40.deg., stirring 3 hr at 40.deg. and 2 hr at 125-30.deg./10-25 mm, adding 1150 g diethyl phosphite [762-04-9] and 8 g NaOMe, heating 16 hr at 50.deg./5-20 mm with addition of 5 g NaOMe every 2 hr and distillation of EtOH, adding 440 g acrylonitrile [107-13-1] and 30-40g of 33% NaOMe over 45 min, and stirring 30 min at pH 7-9 gives 2080 g crude 2-(carbamoyloxy)ethyl ethyl (2-cyanoethyl)phosphonate (I) [52870-25-4]. Addition of I over 10 min to 740 g 37% HCHO [50-00-0] and .sim.10 g 33% NaOH and stirring 1 hr at 40-50.deg. and pH 9-10 gives 2900 g aqueous N-methylol derivative (II) [52870-36-7] of I. Cotton fabric (320 g/m2) is padded to 75% uptake with a solution containing II 350, hexamethylolmelamine pentamethyl ether 40, and NH4Cl 4 g/l., dried to 6% residual moisture at 120.deg., and cured 4 min at 170.deg. to give a product which remains fire resistant (DIN 53 906) after 15 launderings.

ACCESSION NUMBER: 1974:554487 CAPLUS
DOCUMENT NUMBER: 81:154487
TITLE: Phosphorus compounds containing carbamate groups and their use as flame-protective additives
INVENTOR(S): Duersch, Walter; Linke, Fritz; Beermann, Claus; Nischwitz, Ehrenfried
PATENT ASSIGNEE(S): Farbwerke Hoechst A.-G.
SOURCE: Ger. Offen., 42 pp.
CODEN: GWXXEX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2249321	A1	19740502	DE 1972-2249321	19721007
DE 2249321	B2	19751030		
DE 2249321	C3	19760610		
CH 7314160	A4	19750415	CH 1973-14160	19731004
CH 567145	B	19750930		
CH 565810	A	19750829	CH 1975-2118	19731004
JP 49070951	A2	19740709	JP 1973-111603	19731005
US 3876601	A	19750408	US 1973-404096	19731005
AT 7308508	A	19750615	AT 1973-8508	19731005
AT 328409	B	19760325		
IT 995655	A	19751120	IT 1973-29825	19731005
GB 1429545	A	19760324	GB 1973-46598	19731005
CA 1000276	A1	19761123	CA 1973-182767	19731005
BE 805772	A1	19740408	BE 1973-136429	19731008
FR 2202100	A1	19740503	FR 1973-35832	19731008
PRIORITY APPLN. INFO.:			DE 1972-2249321 A	19721007

L7 ANSWER 17 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Compns. were prepared, which are useful in the treatment of leather, paper, glass, plastic, rubber, wood, and textiles, from water soluble or water dispersible salts of polyurethane resins, surfactants, epoxides, pigments, and solvents. The polyurethane resins were obtained by reacting an isocyanate terminated prepolymer with a OH containing N compound which is the Mannich condensation product of a phenol, an aldehyde, and an alkanolamine. Thus, a OH-containing N compound was prepared as follows: a mixture of 315 g. (HOCH2CH2)2NH and 60 g. MeOH was cooled to 10°C., 244.5 g. 37% HCHO was added with stirring over 60 min., a mixture of 282 g. PhOH and 25 g. MeOH was added over 15 min. at 18-22°C,. the mixture was stirred for 1 hr. at 18-22°C., heated to 65°C., stirred for 2 hrs. at 65°C., and the mixture was subjected to vacuum distillation to a pOt temperature of 100°C. for 15 min. An isocyanate-terminated prepolymer was prepared as follows: 812 g. polyethylene glycol 1540 was added in 30 min. with agitation to 199 g. tolylene diisocyanate under N while maintaining the reaction temperature at 45-55°C. and the mixture was heated for 1 hr. at 80-5°C. To 500 g. melted prepolymer was added 105.5 g. of the OH containing N compound, the mixture was heated 90 min. at 90-5°C., cooled to 70°C., and a solution of 30 g. HOAc in 635.5 g. H2O was added to give a treating agent composition (I). A chrome tanned shaved side leather was put in a drum, 100 weight % water was added, the leather was washed at 100°F., drained, floated with 50 weight % water, heated to 100°F., 4% I was added, the mixture was agitated 1 hr., a solution at 100°F. containing 5% of a condensation product of urea, HCHO, and sulfonated cresol and 50% water based on the weight of the leather was added to the leather, the mixture was agitated 1 hr., drained, the leather washed 10 min. at 125°F. with water, drained, and fat-liquored for 45 min. at 125°F. with 5% sulfated vegetable and animal oils. The leather was pulled, horsed, and dried; the leather showed a tight grained effect and excellent temper. Other alkanolamines used in the preparation of the OH containing N compound were monoethanolamine, N-methylmono-ethanolamine, N-ethylmonoethanolamine, and N-benzyldi-ethanolamine. Other prepolymers used were prepared from polypropylene glycol and tolylene diisocyanate. Other phenols used in the preparation of the OH containing N compound were nonylphenol and bisphenol A; 4,4'-dihydroxydiphenylmethane was also claimed. The treating agent compns. were also used as pigment binders on fiber glass fabrics and glass fabrics were also coated with the treating compns. and then dyed. The treating agents also decreased the capacity of Dacron fabrics to retain electrostatic charges and improved the abrasion resistance of cotton fabrics. The treating agent was also used to bond glass fibers to a resorcinol-hCHO latex coating and as a tie bond coating for glass fiber roving.

ACCESSION NUMBER: 1969:482777 CAPLUS
DOCUMENT NUMBER: 71:82777
TITLE: Urethane composition
INVENTOR(S): Sellet, Lucien
PATENT ASSIGNEE(S): Diamond Alkali Co.
SOURCE: U.S., 29 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

L7 ANSWER 17 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3462237	A	19690819	US 1965-475600	19650728
PRIORITY APPLN. INFO.:			US 1965-475600 A	19650728

L7 ANSWER 18 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Condensation products of an aromatic amine with an aliphatic or aromatic aldehyde are cast, brushed, or sprayed as solution or dispersion on an elec. conductive support to obtain transparent photoconductive layers which are charged, exposed, and developed with a toner powder fusing at 110-125°, as are conventional materials. Impregnation of a paper base to inhibit penetration by the solution is unnecessary. The unexposed coatings are removable by dilute acids in the preparation of printing plates.

Dyes can be added as optical sensitizers and electron acceptors with a mol. weight between 100 and 1000 and an absorption maximum in the uv range as activators. N-Ethylaniline and HCHO are condensed by a 2-stage process. In the first, N,N'-diethyl-N,N'-diphenylmethylenediamine, m. 79°, is produced by stirring for 3 days at room temperature a mixture of N-ethylaniline 726 parts by weight, 40% HCHO 225 parts by weight, and 2N NaOH 3 parts by volume The filtered reaction product 245 parts by weight, HCHO 90 parts by volume, and HCl 240 parts by volume are heated 6 hrs. on a steam bath, and the condensate is isolated as amber-yellow resin distn. residue, softening at 90-100°, after adjustment of the pH to >7 by aqueous Na2CO3, and extraction with CHCl3. A paper printing foil is coated with 2 parts by weight resin in 30 parts by volume EtOAc and 1 part 1% Rhodamine B solution After processing the plate, the resin is removed from areas not covered by resinous toner by wiping with 5% H3PO4 and rinsing with water, whereby the hydrophilic paper is bared for use as a printing plate.

ACCESSION NUMBER: 1966:100028 CAPLUS
DOCUMENT NUMBER: 64:100028
ORIGINAL REFERENCE NO.: 64:18786b-d
TITLE: Amine-aldehyde resins as photoconductors for electrophotographic processes
INVENTOR(S): Lind, Erwin
PATENT ASSIGNEE(S): Azoplate Corp.
SOURCE: 4 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3244517		19660405	US	
PRIORITY APPLN. INFO.:			DE	19600917

L7 ANSWER 19 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Aromatic amines, such as aniline, m-methylaniline and o-chloroaniline (I), are condensed with H2O at >105° in the presence of an acid catalyst in an amount of 0.15.0 mole %, based on the aromatic amine; 1.5-10 moles aromatic amine per mole H2CO are used. The acid catalysts have a pKA ≤3 and are monobasic protonic acids, such as HCl or methanesulfonic acid, or Lewis acids, which are hydrolyzed in water to give monobasic protonic acids. The aromatic polyamines thus obtained have a higher proportion of o-CH2 linkages, a lower m.p., and a lower viscosity than the known aromatic amine -H2CO condensates, prepared at lower temperature in the presence of greater amts. of acid. A higher reaction temperature results in a higher proportion of ortho linkages. The polyamines can be used as curing agents in the production of polyurethan elastomers and polyepoxide resins. The polyamines can be phosgenated to low-melting polyisocyanates, e.g. liquid bis(isocyanatophenyl)methane, which are very suitable for the preparation of polyurethan resins and foams. Polyols obtained by the reaction of the polyamines with epoxides, such as propylene oxide, are also useful for this purpose. Thus, a mixture of 117.5 moles I and 0.905 mole of a mixed alkanesulfonic acid was heated to 130°, and 29.75 moles H2CO (in the form of a 37% aqueous solution) were added over a period of 345 min. During this period, the temperature was kept at 130-5° and H2O was distd. After the addition, the reaction mixture was kept at 130-5° for 2 hrs. The pressure was then gradually reduced in 5 hrs. to a min. of 4 mm. This pressure was held for 30 min.; yield 7420 g. polyamine. The polyamine was ion-exchanged to remove the catalyst. It was liquid at room temperature and contained 74.2% by weight diamine. The diamine contained 25.3% 2,4'-, 72.6% 4,4'-, and 2.1% 2,2'-diamino-3,3'-dichlorodiphenylmethane.

ACCESSION NUMBER: 1965:472875 CAPLUS
DOCUMENT NUMBER: 63:72875
ORIGINAL REFERENCE NO.: 63:13504g-h,13505a-b
TITLE: Low-melting aromatic polyamines obtained by condensation of aromatic antines with formaldehyde
PATENT ASSIGNEE(S): Union Carbide Corp.
SOURCE: 46 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 6406403		19641207	NL	
PRIORITY APPLN. INFO.:			US	19630606

L7 ANSWER 20 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB Organic photoconductive resins in the table were prepared by condensing an aldehyde with a substituted or unsubstituted aromatic amine: Amine, Adehyde, Color, Softens, Soluble; 4-FC6H4NH2, H2CO, brown, 70-80°, EtOAc; 4-BrC6H4NH2, H2CO, brown, 110-20°, EtOAc; 4-ClC6H4NH2, H2CO, brown, --, EtOAc; PhNHEt, H2CO, amber yellow, 90-100°, --; PhNHPr, H2CO, dark yellow, --, EtOAc; PhNHBu, H2CO, dark yellow, --, EtOAc; 2-C10H7NH2, H2CO, brown, 60-65°, --; 1-C10H7NHEt, H2CO, dark brown, 55°, EtOAc; m-MeC6H4NHMe, H2CO, dark yellow, 90°, EtOAc; p-MeC6H4NHEt, H2CO, brown, 102°, --; 1-C10H7NH2, MeCHO, brown, 80°; --; o-MeC6H4NH2, MeCHO, dark yellow, 60-80°, EtOAc; PhNH2, crotonaldehyde, brown, --, EtOAc; 1-C10H7NH2, crotonaldehyde, brown, 100-70°, EtOAc; o-MeC6H4NH2, crotonaldehyde, brown, 100-20°, --; PhNHEt, crotonaldehyde, brown, 100°, --; 1-C10H7NHEt, crotonaldehyde, brown, 100°, --; PhNH2, furfural, dark brown, 75-90°, HCON Me2; PhNHEt, furfural, dark brown, 75-90°, --; A solution or dispersion of one of these photoconductive resins may be applied to an elec. conducting support to form a photoconductive coating. These materials may be applied to untreated paper supports without undue penetration of the paper by the coating solution The light sensitivity of the coatings may be increased by incorporation of known optical sensitizers and also by incorporation of a small quantity of an activator; other additives such as plasticizers, resins, and dyes may be included. The coatings are soluble in acids, facilitating preparation of printing plates from developed images. The coatings (if unpigmented) are transparent, so the developed prints may be reproduced by transmittance processes if the support used is transparent. For example, a condensation product was prepared by heating 364 parts by weight of m-MeC6H4NHMe, 160 parts by weight of 40% H2CO solution, and 120 parts by volume of concentrated HCl for 6 h. on a steam bath, the solution was made alkaline by adding Na2CO3, then the resin was isolated by extraction with CHCl3, drying with K2CO3, and distillation of the CHCl3; 7 parts by weight of this condensation product were dissolved in 30 parts by volume of EtOAc, and the solution was applied to a transparent paper. After drying, an image was produced by the electrophotog. process, developed by powder treatment, and fixed by heat, yielding a transparent intermediate original suitable for the preparation of further copies, e.g. by photoprinting.

ACCESSION NUMBER: 1965:48389 CAPLUS
DOCUMENT NUMBER: 62:48389
ORIGINAL REFERENCE NO.: 62:8570b-f
TITLE: Electrophotographic material
PATENT ASSIGNEE(S): Kalle A.-G.
SOURCE: 5 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 977399		19641209	GB	
DE 1197325			DE	
PRIORITY APPLN. INFO.:			DE	19600917

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GI For diagram(s), see printed CA Issue.

AB In neutral or weakly acid solution, C-N bonds only were formed in reactions between HCHO (I) and aromatic amines. Thus, 8-nitro-1-naphthylamine condensed with I in AcOH gave an almost theoretical yield of dihydro-5-(8-nitro-1-naphthyl)-4H-1,3,5-dioxazine, m. 175° (Morgan and Jones, CA 17, 1960). I (50 ml.) warmed with 5 g. p-H2NC6H4Ac until a clear solution was formed gave 2.1 g. II (R = p-AcC6H4), m. 220-1° (decomposition) (xylene). II (R = m-O2NC6H4), m. 224° (decomposition), and II (R = p-O2NC6H4), m. 280-2° (decomposition), were prepared similarly. Reactions between I and certain p-substituted aromatic amines in acid solution produced both new C-C and C-N bonds, and the benzene ring was involved in the reactions. Formation of certain compds. appeared to be capricious, and the products of a reaction were determined largely by the concentration of the reactants. Thus, 62 g. p-MeOC06-H4NH2, 200 ml. 5N HCl, and 70 ml. 40% I kept 2 days gave 26 g. III (R = OMe) (IV) HCl salt; IV m. 172°. The filtrate from IV diluted to 1 l., the mixture kept 1 day and filtered, and the precipitate digested with 50 ml. cold EtOH afforded 5 g. V (R = OMe) (VI), m. 215° (H2O), and 12.5 g. EtOH-soluble VII (R = OMe, R' = H) (VIII); HCl salt m. 110° (decomposition). Basification with NH4OH to pH 8 of the filtrate from VI and VIII.HCl precipitated an oil, and saturation with NaCl of the supernatant liquid produced 10g. IX(R =OMe); picrate m. 204°. The precipitated oil dissolved in 100 ml. 2N HCl gave 10 g. 3-p-anisyl-3,4-dihydro-6-methoxyquinazoline (X)hydrochloride; X m. 136°; methiodide m. 220°. Addition of alkali to the filtrate from X.HCl produced <0.5 g. XI(R = OMe) (XII), m. 156° (Me2CO); picrate m. 140-2°. Basification of VI produced either 5,2-R(MeNH)C6H3CH2N-(CHO)C6H4R-p (XIII) (R = OMe) or 5,2-R(OHCNMe)C6H3CH2NHC6H4R-p (XIV) (R =OMe), m. 121,° picrate m. 165°. Oxidation with H2O2 of the corresponding VI iodide gave unstable XV (R = OMe), m. 134°. Reduction of VIII, m. 128° [dipicrate m. 180°; PhNCO adduct m. 156°; p-toluenesulfonate m. 88° (decomposition); N-nitroso compound m. 116°], with NaBH4 in EtOH produced XII. Other condensations of I with amines in aqueous HCl afforded the following compds: (from p-EtOC6H4NH2) IX (R = OEt), m. 225° (decomposition) [pseudo base m. 150°; picrate m. 197°]; III (R = OEt), m. 133-4°; 6-ethoxy-3-(p-ethoxyphenyl)-3,4-dihydroquinazoline, m. 140°; V (R = OEt) [the corresponding iodide was oxidized by H2O2 to XV (R = OEt), m. 200°]; either XIII or XIV (R = OEt), m. 116°; (picrate m. 166°); 3,9-diethoxy-5,6,11,12-tetrahydro-5,11-dimethylphenhomazine, m. 152°; (from β- naphthylamine) 1,2-dihydro-2-(2-naphthyl)benzo[f]quinazoline, m. 185-7° [picrate m. 256° (decomposition)]; 3 isomeric Troeger bases (N,N'-methanodinaphtho-[1,5]diazocines) of m.ps. 187° 211° and 201°, resp.; dinitroso derivs. m. 255°, 260°, and 247° (decomposition), resp.; (from p-MeC6H4NH2) 1,2-dihydro derivative of VII (R = Me, R' = CHO) (XVI), m. 141° [XVI was originally formulated by Eisner and Wagner (CA 28, 6718d) as 1,2,3,4-tetrahydro-6-methyl-1-(p-toluidinomethyl)-3-p-tolyl-2-quinazolinol] [chloride m. 280° (decomposition); picrate m. 204°]; III (R = Me), m. 136°; VII (R = Me, R' = H), m. 120° (picrate m. 210°; N-nitroso compound, m. 70°); XI (R = Me) [also obtained by NaBH4 reduction XVI), m. 148° (Cellosolve), either XIII or XIV (R = Me) (picrate m. 187-8°; iodide m. 265°) [addition of H2O2 to this iodide XV (R = Me), m. 173-5°]; 3,4-dihydro-6-methyl-3-p-

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tolylquinazoline, m. 166°; (from p-ClC6H4NH2) 6-chloro-3-(p-chlorophenyl)-3,4-dihydroquinazoline, m. 190° p-ClC6H4NMeCH2C6H3(NHCHO)Cl-2,5 [originally formulated by Miller and Wagner (CA 35, 2895d) as 6-chloro-3-(p-chlorophenyl)-3,4-dihydro-1(2H)-quinazolinemethanol], m. 140° (EtOH)(picrate m. 187-8°); (p-ClC6H4NMe)2CH2, m. 117-19°. I (12 ml.), 21 g. o-toluidine, and 110 ml. 98% H2SO4 stirred at 10-20° for 24 hrs. gave XVII (R = NH2, R' = Me) (XVIII), m. 219-20° (xylene). Similarly, 12 g. 0-dianisidine condensed with I in H2SO4 afforded 1.4 g. XVII (R = NH2, R' = OMe), m. 285-6°. XVIII (1 g.) acylated at room temp. with 5 ml. C5H6N and 2 ml. Ac2O produced XVII (R = NHAc, R' = Me), m. >350°, and 1 g. XVIII refluxed 2 hrs. in 10 ml. Ac2O gave 4,4'-diacetamido-5,5'-dimethyl-2,2'-biphenyldimethanol diacetate, m. 279° (decompn.). NaNO2 added to a suspension of 1 g. XVIII in 4 ml. HCl and 36 ml. H2O, and the mixt. treated with KI produced 0.3 g. XVII (R = I, R' = Me), m. 216-17°. Reaction of I with arylamines having a free p-position in acidified Na2S2O3 soln. gave derivs. of [3,4-R2(RR1N)C6H3CH2]2Sn (XX) and (PhCH2)2S. Thus, 25 g. Na2S2O3, 25 ml. H2O, and 8 ml. 40% I added to 10 g. PhNH2 and 50 ml. 5N HCl and the mixt. heated 4 hrs. at 100° gave 7-9.5 g. XX.2HCl (R, R1, R2 = H, n = .apprx.4), m. 240° (decompn.), and 4 g. (p-H2NC6H4CH2)2S, m. 103-5°. Similarly, condensations using o-MeC6H4-NH2, PhNHMe, and PhNMe2 produced XX.2HCl (R = R1 = H, R2 = Me, n = 4), m. 225° (decompn.) (free base m. 139°) [and [3,4-Me(H2N)C6H3CH2]2S m. 155°], XX (R = R2 = H, R1 = Me, n = 1), m. 55° (dinitroso deriv. m. 136°), and (p-Me2NC6H4CH2)2S (XXI), m. 62°, resp. XXI distd. at 11 mm. decompd. to H2S, p-MeC6H4NMe2, and P-Me2NC6H4CH:CHC6H4NMe2-p. XXI refluxed 30 min. with Cu-bronze and 1,2,4-trichlorobenzene produced p-Me2NC6H4CH2CH2C6H4NMe2-p.

ACCESSION NUMBER: 1965:43896 CAPLUS
DOCUMENT NUMBER: 62:43896
ORIGINAL REFERENCE NO.: 62:7753c-h,7754a-e
TITLE: Reactions of formaldehyde with aromatic amines
AUTHOR(S): Farrar, W. V.
CORPORATE SOURCE: Univ. Manchester, UK
SOURCE: Journal of Applied Chemistry (1964), 14(9), 389-99 CODEN: JACHAU; ISSN: 0021-8871
DOCUMENT TYPE: Journal
LANGUAGE: English

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AB To a cooled solution of 500 g. 40% aqueous MeNH2 was added 258 g. 2-(N-benzyl-N-methylamino)ethyl chloride hydrochloride and the mixture stirred 1 hr. at room temperature The mixture was heated at 80-90° 3 hrs., cooled, treated portionwise with 200 g. NaOH, and extracted with Et2O to give 137 g. N-benzyl-N,N'-dimethylethylenediamine (I), b0.5 .apprx.80-2°. A solution of 175 g. I in 500 ml. CHCl3 was added dropwise to a solution of 261 g. α-chlorodiphenylacetyl chloride in 1 l. CHCl3 at 20-5°. The mixture was refluxed 1 hr., then treated dropwise with 500 ml. absolute EtOH while distilling 1400 ml. solvent. The residue was refluxed 8 hrs. with 1500 ml. absolute EtOH to give 427 g. N-[2-(N'-benzyl-N'-methylamino)ethyl]-2-ethoxy-N-methyl-2,2-diphenylacetamide; hydrochloride (II) m. 162-4° (MeCNEt2O). A warm solution of 35 g. II was treated with a suspension of 3 g. 5% Pd-C at 55 lb.-30 min. to give 24.7 g. 2-ethoxy-N-methyl-N-(2-methylaminoethyl)-2,2-diphenylacetamide; hydrochloride (III) m. 202-3° (absolute EtOH). A suspension of 25 g. III and 200 ml. H2O was treated with 3 g. NaOH in 30 ml. H2O and the mixture extracted with Et2O to give 19.5 g. 2-ethoxy-N-methyl-N-(2-methylaminoethyl)-2,2-diphenylacetamide (IV), m. 458°. A mixture of 12.0 g. IV, 5.7 g. phenacyl chloride, and 250 ml. xylene was refluxed 15 min., cooled, and filtered and the filtrate treated with 4 ml. 5N alc. HCl to give 7 g. 2-ethoxy-N-methyl-N-(2-methylphenacylamino)ethyl-2,2-diphenylacetamide; hydrochloride (V) m. about 187-8°. A suspension 4.1 g. V in 20 ml. 50% EtOH was treated with 0.4 g. NaOH in 30 ml. 95% alc. followed by 0.4 g. NaBH4. The mixture was stirred 10 min., then extracted with ether, and the ether extract treated with 2 ml. alc. HCl to give 3.5 g. 2-ethoxy-N-[2-[(β-hydroxyphenethyl]methylamino]ethyl]-N- methyl-2,2-diphenylacetamide hydrochloride (VI), m. 162-4°. VI was also prepared by treating IV with styrene oxide. 2-Ethoxy-N- [2-[(β-hydroxy-4-nitrophenethyl)methylamino]ethyl]- N-methyl-2,2-diphenylacetamide hydrochloride was hydrogenated to give N- [2- [p-amino-β-hydroxyphenethyl)methylamino]ethyl]-2-ethoxy-N-methyl- 2,2- diphenylacetamide; dihydrochloride m. about 130-2°. The title compds. are useful as analgesics.

ACCESSION NUMBER: 1964:468972 CAPLUS
DOCUMENT NUMBER: 61:68972
ORIGINAL REFERENCE NO.: 61:11938b-f
TITLE: Diphenylacetamide derivatives
INVENTOR(S): Krapcho, John
PATENT ASSIGNEE(S): Olin Mathieson Chemical Corp.
SOURCE: 3 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3143555		19640804	US	19620305

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GI For diagram(s), see printed CA Issue.
AB A mixture of 50 g. aniline, 20 g. paraformaldehyde in 100 ml. 80% MeOH, and 5 g. AcONa was heated 2 hrs. at 60°, kept overnight, and filtered to give 40 g. condensate (I). I (40 g.) in 100 ml. C6H6 was boiled and the mixture filtered and cooled to give 25 g. II, m. 140° (C6H6). To a mixture of 38 g. aniline, 10 g. EtOH, and 10 g. KOH was added 6 g. paraformaldehyde with stirring. The mixture was stirred 2 hrs. at 60-70°, kept overnight, and filtered to give (PhNH)2CH2 (III), m. 64-5° (iso-Pr2O). The benzene-insol. portion of I was washed with C6H6 and CHCl3 to give 3 g. (N(Ph)CH2]n (IV), m. 208°. II or IV (10 g.) in 50 ml. MeOH of C6H6 was hydrogenated (80 atmospheric H for 8 hrs. at 80°) and filtered. Ac2O was added to the reduction product and the mixture heated 1 hr. at 60°, cooled, and filtered to give acetanilide, m. 114° (MeOH). The filtrate was distilled and separated into 2 fractions (V and VI), b4 52-6° and b4 102-5°, resp. V was identified as N,N-dimethylaniline as follows: V was heated with MeI to give PhMe3NI, m. 211° (MeOH). Cooling of VI gave N-methylacetanilide, m. 105° (MeOH). Similarly, catalytic reduction of III gave a 1:1 mixture of PhNH2 and PhNHMe.

ACCESSION NUMBER: 1963:435276 CAPLUS
DOCUMENT NUMBER: 59:35276
ORIGINAL REFERENCE NO.: 59:6280g-h,6281a
TITLE: Catalytic reduction of aniline-formoldehyde condensates
AUTHOR(S): Wakae, Masao; Konishi, Kenzo
CORPORATE SOURCE: Ind. Res. Inst., Osaka, Japan
SOURCE: Osaka-furitsu Kogyo Shoreikan Hokoku (1963), No. 29, 47-50
CODEN: OFKSAN; ISSN: 0369-7223
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Compds. 1,2-BrC10H6SX, where X = Cl (I), SCN (II), H2CCOMe (III), CH2COPh (IV), 4-HOC6H4 (V), 2,4-(HO)2C6H3 (VI), 4,1-HOC10H6 (VII), 2,1-HOC10H6 (VIII), NH2 (IX), PhCH:N (X), PhNH (XI), 1-C10H7NH (XII), 4,1-H2NC10H6 (XIII), 2-C10H7NH (XIV), 2,1-H2NC10H6 (XV), 4-Me2NC6H4 (XVI), 4-Et2NC6H4 (XVII), cyano (XVIII), AcO (XIX), and 1,2-BrC10H6SO2 (XX) were prepared; also R2NH (XXI), 1,2,4-H2NC10H6R2 (XXII), 1,2-RC10H6NHR (XXIII), and R2O (XXIV) (R = 2-C10H7S). 1-Bromo-2-naphthylsulfinic acid, m. 135° (Cohen and Smiles, CA 23, 2172), was obtained in 86% yield. Bis(1-bromo-2-naphthyl)disulfide (4.76 g.) in CCl4 treated with 0.8 g. anhydrous Cl, then filtered, and the filtrate concentrated gave 96% I, m. 93-4° (decomposition). I (2.73 g.) in 40 ml. C6H6 treated with 1.45 g. anhydrous KSCN 1 hr. at 25-30° gave quant. II, m. 77-8° (petr. ether). I (1.36 g.), treated with 20 ml. anhydrous Me2CO, gave quant. III, m. 72-3° (petr. ether). III was also obtained from II and Me2CO, after 24 hrs. at room temperature I (1.36 g.) in C6H6 treated with 3 ml. PhCOMe and the excess steam distilled, gave 80% IV, m. 120-20.5° (petr. ether). II gave also with PhCOMe after 24 hrs. at room temperature IV in 74% yield. I (1.4 g.) treated with freshly distilled PhOH, then with dilute NaOH, the insol. filtered off, the filtrate precipitated with dilute H2SO4, filtered off, and recrystd. gave 41% V, m. 107.8-9° (petr. ether). The acetate, m. 92.8-4.2° (petr. ether), was obtained with Ac2O and concentrated H2SO4. I (2.04 g.) in 30 ml. CHCl3 added to 0.92 g. resorcinol in 3 ml. anhydrous Et2O, the excess removed with boiling H2O gave 90% VI, m. 157-8.4° (C6H6-petr. ether). This gave with Ac2O and concentrated H2SO4 the diacetate, m. 92.4-3.6° (petr. ether), in 87% yield. VI was also obtained in 90% yield from II and resorcinol after 48 hrs. at room temperature I (1.3 g.) added to α-naphthol in C6H6 gave 93% VII, m. 131.5-2.3° (petr. ether); acetate m. 136-6.8° (petr. ether). Attempts to condense II with α-naphthol failed. β-Naphthol (1.08 g.) added to 2.04 g. I in 15 ml. C6H6 gave 91% VIII, m. 155-6° (petr. ether); acetate m. 119-20° (petr. ether). I dissolved in CHCl3-Et2O and treated with anhydrous NH3 gave IX, but the crude product was very difficult to purify. II (4.8 g.) in Et2O-CHCl3 solution treated with ethereal NH3, the solvent removed, and the residue crystallized from petr. ether, gave 90% IX, decomposed at 90-205°. BzH (0.60 g.) added to 1.47 g. IX in 150 ml. MeOH gave in 70% yield X, m. 114.4-15° (MeOH). I (1.36 g.) in 20 ml. C6H6 treated with 0.93 g. PhNH2 in 5 ml. C6H6 gave 97% XI, m. 129-30° (petr. ether). I (2.73 g.) in 30 ml. C6H6 was added to α- naphthylamine (2.86 g.) in 20 ml. C6H6, filtered, and the filtrate evaporated to an oily residue which gave 75% XII, m. 138-9° (decomposition) (petr. ether). II (1.48 g.) added to 1.43 g. α- naphthylamine, in 40 ml. C6H6, filtered, and the filtrate evaporated, to an oily residue, which was crystallized from C6H6-petr. ether to give quant. XIII (isomer of XII), m. 157.2-9.2° (MeOH). I (1.36 g.) in 20 ml. C6H6 added to 1.43 g. β- naphthylamine in 10 ml. C6H6, then concentrated gave in 95% yield XIV, m. 137-8° (C6H6-petr. ether). XV.HCl was obtained in 89% yield from 3.23 g. I in 200 ml. AcOH treated with 1.69 g. β-naphthylamine in 15 ml. AcOH. This, triturated with EtOH and 10% Na2CO3 gave the base, m. 199.2-200.4° (C6H6-petr. ether). II (0.74 g.) added to 0.72 g. β- naphthylamine in 40 ml. C6H6, then concentrated gave 97% XV. XV in 48% yield was obtained from 0.37 g. I in 20 ml. AcOH and 0.18 g. β- naphthylamine, 48 hrs. at room temperature

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XVI, m. 136.8-7.8° (petr. ether), was obtained in 99% yield from 2.04 g. I and 2.30 g. PhNMe2 in C6H6 soln., then treated with 5 ml. 10% Na2CO3, and the excess PhNMe2 steam distd. XVI was also obtained from II and PhNMe2. PhNEt2 (1.87 g.) added to 1.36 g. I in 15 ml. C6H6 gave a ppt. This and the soln. were treated with 5 ml. 5% Na2CO3 and the excess of reagents steam distd. to give 99% XVII, m. 140.2-0.9° (petr. ether). XVII was also prepd. from II and PhNEt2. I (1.0 g.) or II in 20 ml. EtOAc treated with excess KCN, then with AcOH (10 ml.) gave XVIII, m. 142.8-3.8° (petr. ether). XIX, m. 44-8°, was obtained in 52% yield from 1.66 g. AgOAc suspended in 10 ml. abs. MeOH treated with 1.36 g. I, stirred 1 hr., then filtered, and the filtrate concd. 1-Bromo-2-naphthylsulfinic acid in NH4OH, treated with aq. AgNO3 gave the silver salt of the sulfinic acid. This (1.49 g.), suspended in C6H6 added to 1.02 g. I in C6H6 gave AgCl ppt., which was filtered off, and the filtrate concd. to give 73% XX, m. 174-5° (C6H6-petr. ether). XXI was obtained quant. from 1.0 g. IX treated with 50 ml. AcOH, m. 208-9° (decompn.) (C2H2Cl4-C6H6). XXII.HCl was obtained in 86% yield from 2.06 g. I in 150 ml. AcOH treated with 0.54 g. α- naphthylamine in 20 ml. AcOH. This, triturated with 10% Na2CO3 gave XXII, m. 239-40° (decompn.). XXII diacetate was obtained from XXII treated with Ac2O-NaOAc, m. 189-92.5° (CCl4-petr. ether). XIII (0.95 g.) in 15 ml. C6H6 treated with 0.74 g. II in 10 ml. C6H6, left several days at room temp., and the solvent evapd., gave in 98% yield XXII. XIII (0.47 g.) in 50 ml. C6H6 treated with 0.77 g. I in 10 ml. C6H6, gave after 3 days XXII. XXII in 98% yield, was prepd. from 0.95 g. XIII in 30 ml. AcOH and 0.68 g. I in 50 ml. AcOH. The hydrochloride obtained, treated with MeOH and 10% Na2CO3 liberated the base. I (0.68 g.) in 70 ml. AcOH treated with 0.71 g. α-naphthylamine in 20 ml. AcOH gave after 2 days at room temp. 31% XXII. XV (2.84 g.) in 40 ml. C6H6 added to 1.02 g. I, then filtered, and the filtrate concd., gave quant. XXIII, m. 186-7° (decompn.) (C6H6-petr. ether). XXIV, m. 146° (decompn.), was obtained in 90% and 66% yield resp. from 2.0 g. I and II, resp., in 60 ml. petr. ether stirred with N Na2CO3, and the obtained ppt. filtered off and dried. To prove the reactivity of some of synthesized compds. the following reactions were run. XII (0.5 g.) suspended in 15 ml. CCl4, treated with anhyd. HCl gave quant. α- naphthylamine-HCl. This was filtered off and the filtrate concd. Half of the residue dissolved in AcOH, treated with KI aq. soln., liberated iodine. The remainder treated with Me2CO gave III. II, treated with 10% NaOH gave bis(1-bromo-2-naphthyl) disulfide. This was filtered off and from the filtrate, treated with dil. H2SO4, was obtained 1-bromo-2-naphthylsulfinic acid. XXIV (0.5 g.) moistened with EtOH, treated with 5 ml. N NaOH, gave a ppt. which was filtered off and recrystd. from CCl4 to give bis(1-bromo-2-naphthyl) disulfide. The filtrate treated with dil. H2SO4 gave 1-bromo-2-naphthylsulfinic acid.

ACCESSION NUMBER: 1963:3155 CAPLUS
DOCUMENT NUMBER: 58:3155
ORIGINAL REFERENCE NO.: 58:485a-h,486a-c
TITLE: Reactivity of 1-bromo-2-naphthalenesulfenyl chloride and thiocyanate
AUTHOR(S): Pitombo, Luiz R. M.
CORPORATE SOURCE: Univ. Sao Paolo, Brazil
SOURCE: Univ. Sao Paulo, Fac. Filosof., Cienc. Letras, Bol. Quim. (1959), (No. 5), 39-73
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Products containing the group R'N[CH2CH(R)O]nH, in which R is H or Me, R' is an alkyl, cycloalkyl, aryl, or aralkyl group, and n is 1-10, are made as described in the main patent. Thus, 538 g. tetraethoxyaniline, 151 g. N-methyl-N-hydroxyethylaniline, and 100 g. paraformaldehyde were heated to 80-90° under CO2. Then 8 g. H3PO4 was added slowly, whereupon the aldehyde was dissolved. After 1-2 hrs. at 80-90°, all H2O was distilled off in a vacuum, and the condensation was continued until the desired viscosity was obtained. The product was a dark oil with a OH number of 369 and a viscosity of 496 cp. at 75°. N-Butyl-N-hydroxyethylaniline was also used, and p-toluenesulfonic acid may be used as a catalyst.

ACCESSION NUMBER: 1961:40739 CAPLUS
DOCUMENT NUMBER: 55:40739
ORIGINAL REFERENCE NO.: 55:7922i,7923a
TITLE: Condensation polymers
INVENTOR(S): Muller, Erwin; Bayer, Otto
PATENT ASSIGNEE(S): Farbenfabriken Bayer Akt.-Ges.
SOURCE: Addn. to Ger. 1,048,411 (CA 55, 2201a)
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1060140		19590625	DE	

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AB The reactions of 2-substituted primary and secondary furfurylamine derivatives with HCHO were shown to produce hexahydrotriazines and methylenediamines, resp.; tertiary furfurylamines and their alkyl halides reacted with Ac2O to give furfuryl acetates. Furfurylamine (I), b17 54-6°, n20D 1.4908 (I picrate m. 177.5-8.5°), was prepared in 70% yield by refluxing 17 g. furfural oxime, 12 g. Al (as Al-Hg), and 300 ml. EtOH 5 hrs., filtering off Al(OH)3, adding 60 ml. 3N HCl, distilling, adding 30 ml. 30%, NaOH, extracting with Et2O, drying over solid KOH, distilling, and fractionating the residue. A mixture of 9.7 g. I and 8.0 g. 37% HCHO was heated on a water bath 2 hrs., extracted with Et2O, and distilled to yield N,N',N''-trifurfurylhexahydrotriazine. The Schiff base prepared from 20 g. furfural (II) and MeNH2 was reduced in EtOH 10 hrs. by Na-Hg. After removal of the Hg, the mixture was steam-distilled, and 20 ml. concentrated HCl added to the distillate. Unreacted II was removed by steam distillation, the residue made strongly alkaline with NaOH, extracted with Et2O, dried over solid KOH, distilled, and fractionated to yield 68% N-methylfurfurylamine (III), b69 79-80°, n20D 1.4729; III.-HCl, m. 144.5-6.0°; III picrate, m. 143.5-4.5°. Methylenebis(N-methylfurfurylamine) (IV) (79%), b6 126-8°, d20 1.0450, n20D 1.5017, was prepared from 8 g. 37% HCHO and 11 g. II. IV, on steam distillation with picric acid and EtOH, gave quant. yields of HCHO and III picrate. N,N-Dimethylfurfurylamine (V), b73 72-4°, n20D 1.4609, was prepared in 69% yield by the reaction of a mixture of 58 g. HCONMe2 and 25 g. 80% HCO2H with 20 g. II in 60 g. HCO2H; V picrate, m. 101-2°. V (10 g.) was refluxed on a H2O bath 3 hrs. with 10 g. Ac2O, cooled, added to 100 ml. H2O, and neutralized with Na2CO3 to form 87% furfuryl acetate (VI), b21 70-3°, n20D 1.4627. Similarly, VI was obtained from N,N,N-trimethylfurfurylammonium iodide with Ac2O and NaOAc. Attempted reaction of V.HCl with HCHO did not yield condensation product; the higher the temperature, the smaller the amount of unreacted V recovered, and the greater the amount of resinous product formed. MeNH2.HCl (65 g.), 41 g. 2-methylfuran (VII), and 50 g. 37% HCHO gave 24.6% N,5-dimethylfurfurylamine (VIII), b6.5 51-5°, d20 0.9762, n20D 1.4803 (VIII.HCl, m. 140.5-1.5°; VIII picrate, m. 155.5-7.0°), 4.8% bis(5-methyl-2-furyl)methane (IX), b6.5 90-3°, d20 1.0424, n20D 1.5018, 43.8% N-methyl-bis(5-methylfurfuryl)amine (X), b6.5 129-32°, d20 1.0302, n20D 1.5040 (X picrate, m. 91-3°), and traces of methylenebis(N,5-dimethylfurfurylamine) (XI), b6.5 141-4°, d20, 1.0112, n20D 1.4998 (XI picrate, m. 155-6°). XI was prepared from IV and HCHO in 73% yield. Reaction of XI with picric acid gave quant. yields of HCHO and VIII picrate. The reaction of 20 g. VII with 25 g. HCHO and 25 g. Me2NH.HCl gave 72.8% N,N,5-trimethylfurfurylamine (XII), b28 70-3°, n20D 1.4620; XII picrate, m. 115-16°; N,N,5-trimethyl-N-methylfurfurylammonium iodide, m. 160-2°. N,N,5-Trimethyl-N-ethylfurfurylammonium bromide (XIII), m. 130-2° (EtOH-EtOAc), was prepared in 82% yield by refluxing 7 g. XII, 7 g. EtBr, and 10 ml. EtOH for 2.5 hrs., distilling, and extracting with Et2O. 5-Methylfurfuryl acetate (XIV), b7 81-4°, n20D 1.4669, was prepared in 72% yield by heating XII with Ac2O for 2 hrs. at 92-5°, from XIII, NaOAc, and Ac2O in 86% yield. XII with HCHO gave 85% recovered XII; a resinous product, insol. in H2O or Et2O, was obtained in acid solution III (60 g.), 41 g. VII, 65 g. 37% HCHO, and 150 ml. 65% AcOH was refluxed 4 hrs., 400 ml. 25% NaOH added, the aqueous layer extracted with Et2O, the organic and

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Et2O layers dried over solid KOH, distd., and fractionated to yield 10.7% IX, 72.8% VIII, and 9.2% V. Picric acid with IV gave III picrate. 2,5-Furandimethanol diacetate (XV), m. 62-4° (ligroine), was prepd. in 70% yield by heating 31 g. dimethylaminomethylfurfuryl alc., 4 g. anhyd. NaOAc, and 51 g. Ac2O for 2 hrs. at 100°, neutralizing with Na2CO3, and extg. with Et2O. XV (42.5 g.) was heated at 100° for 2 hrs. with 100 ml. EtOH and 30 g. KOH, 100 ml. H2O added, and the soln. extd. with benzene, dried over K2CO3, distd., and chilled to yield 44.1% 2,5-furandimethanol (XVI), m. 73-4° (ligroine). XVI in acid soln. formed a resinous product insol. in org. solvents. VII (8.2 g.) was added dropwise with stirring to 15 g. HCHO, 1 ml. concd. HCl, and 25 ml. EtOH at 35-40°, stirred for 1 hr., dild. with 100 ml. H2O, and extd. with Et2O. After drying over CaCl2 and distg., 30% IX was obtained. Similarly, 8.2 g. VII, 10 g. 45% AcH, and 2 ml. HCl gave 88% 1,1-bis(5-methyl-2-furyl)ethane, b10 108-10°, n20D 1.4992, also prepd. from 17 g. VII, 28 g. Me2NH.HCl in 100 ml. MeOH, and 25 g. AcH in 43.2%, yield; 48.8% VII was recovered.

ACCESSION NUMBER: 1960:80573 CAPLUS
DOCUMENT NUMBER: 54:80573
ORIGINAL REFERENCE NO.: 54:15349g-i,15350a-g
TITLE: Reactions of furan derivatires and formaldehyde
AUTHOR(S): Tsuboyama, Kaoru; Yanagita, Masaya
SOURCE: Scientific Papers of the Institute of Physical and Chemical Research (Japan) (1959), 53, 318-28
CODEN: SPIPAG; ISSN: 0020-3092
DOCUMENT TYPE: Journal
LANGUAGE: English

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AB N-Arylaminomethyl aryl sulfides (I) and 1,3,5-triaryl-1,5-dithia-3-azapentanes were prepared by condensing primary aromatic amines with HCHO and thiophenols. N-Methylanilines condensed with HCHO and thiophenols to form N-methyl-N-arylaminomethyl aryl sulfides (Ia). Two arylaminoethyl aryl sulfides were prepared by condensing β-chloroethylaniline (II) with Na salt of the thiophenol. Basicities of these arylaminoalkyl aryl sulfides were related to the presence of electrophilic substituents attached to the aryl groups and the number of C atoms separating the N and S atoms. 2,4,6-Trimethylbenzenesulfonyl chloride reduced with Zn and H2SO4 gave 2,4,6-trimethylbenzenethiol (thiomesitol). Nitrating mesitylene gave the nitro compound, and reduction of this compound gave 77% 2,4,6-trimethylaniline, b. 230-4°. p-Anisidine converted to N-methyl-p-methoxyacetanilide, treated with NaNO2 and HCl to give N-nitroso-N-methyl-p-anisidine, and the nitroso group removed gave N-methyl-p-anisidine. Treating βhydroxyethylaniline with concentrated HCl and SOCl2 in CHCl3 gave a product, m. 155-60°. I (Ar1NHCH2SAr2) were prepared generally with 0.1 mole of the thiophenol, 0.1 mole primary aromatic amine, 0.1 mole 35-40% HCHO, and 20 ml. 95% alc.; the mixture was heated 2 hrs. at 80° refrigerated if crystallization did not occur, the immiscible oil extracted with Et2O, and distilled in vacuo. These compds. were purified by recrystn. from ligroine. In the synthesis involving pentachlorothiophenol, C6H6 or PhMe was used as solvent and paraformaldehyde replaced HCHO. The following results were obtained (Ar1, Ar2, m.p., and % yield given): Ph, Ph, 52-4.5°, 56; Ph, p-ClC6H4, 62-3.5°, 16; p-ClC6H4, p-ClC6H4, 66.2-7.0°, 33; o-ClC6H4, Ph, - (b1 120-2°), 28; o-ClC6H4, p-ClC6H4, 64-5°, 86; m-ClC6H4, p-ClC6H4, 62.5-4.5°, 23; Ph, 2,4,6-Me3C6H2, 68-70.8°, 19; 2,4,6-Me3C6H2, 2,4,6-Me3C6H2, 157-9.2°, 67; p-MeOC6H4, p-ClC6H4, 73.6-5.6°, 21; p-MeC6H4, p-ClC6H4, 113-15°, -; p-O2NC6H4, p-ClC6H4, 139-41.5°, 74; Ph, C6C16, 125-35°, 46 (crude). Ia (Ar1NMeCH2SAr2) were prepared by the same general method as I by condensing 0.1 mole of the thiophenol and 0.1 mole of the N-methylaniline with 0.1-0.17 mole 35-40% HCHO in 20 ml. alc.; the resulting solid products, with the exceptions noted, were recrystd. from ligroine. Ia formed neither picrates nor p-nitrobenzoates. The following Ia were obtained (Ar1, Ar2, m.p., and % yield given): Ph, Ph, 36.4-8°, 71; Ph, p-ClC6H4, 44.6-6.7°, 72; Ph, 2,4,6-Me3C6H2, 51.8-2.8°, 89; Ph, C6C15, 118-21.4°, 91; p-O2NC6H4, p-ClC6H4, 91.8-3.6°, 66; p-MeOC6H4, p-ClC6H4, 56.6-8.2°, 93. 1,3,5-Triaryl-1,5-dithia-3-azapentanes (Ar1SCH2NAr2CH2SAr1) (III) were obtained as follows. Thiophenol (0.1 mole), 0.05 mole PhNH2, 0.1 mole 35-40% HCHO, and 20 ml. alc. heated 2 hrs. at 80° with stirring, the immiscible oils separated (crystallized on standing), and the resulting solids recrystd. from ligroine gave III. The following III were obtained (Ar1, Ar2, m.p., and % yield given): Ph, Ph, 50.2-2.2°, 56; p-ClC6H4, Ph, 60.6-61.4°, 74; p-ClC6H4, p-MeC6H4, 71-4°, - (obtained as a by-product in the preparation of the corresponding I and is probably contaminated). PhCH2NH2 (0.1 mole), 0.1 mole p-ClC6H4SH, and 0.1 mole 35-40° HCHO in 20 ml. alc. gave 8 g. mixture, m. 54-5.6°; picrate m. 81-145°. A small amount of N-benzylaminomethyl p-chlorophenyl sulfide was obtained from the mother liquors, m. 71-3°. β-Chloroethylaniline-HCl (10 g.) and sufficient H2O for solution was treated with 4.1 g. anhydrous K2CO3 and the solution extracted with Et2O. p-Chlorothiophenol (0.06 mole) in 20 ml. alc.

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added to 3 g. Na in 100 ml. alc. and then refluxed 2 hrs. with the filtered soln. of β-chloroethylaniline, the pptd. NaCl removed, the alc. and Et2O evapd., the solid residue dissolved in Et2O, extd. with 200 ml. 10% HCl, the solid floating between the layers sepd., slurried with H2O, treated with 10% NaOH followed by extn. with Et2O, the acid wash H2O treated with 10% NaOH, the solid that sepd. extd. with Et2O, the ext. combined with the other Et2O exts., dried, evapd., the residue dissolved in MeOH, and cooled gave 38% N-phenylamino-ethyl p-cohlorophenyl sulfide, m. 45.2-6.6°; picrate m. 126.8-7.6°. Following the same procedure but using thiophenol gave a yellow oil following the neutralization of the HCl ext. with 10% NaOH; this oil in Et2O dried and evapd. gave 12.1 g. oil, which treated with Nuchar gave 21% N-phenylaminoethyl phenyl sulfide, m. 35-41° (ligroine). Infrared spectra were obtained for a no. of the above compds. The following observations were made from the infrared spectra. In support of the sulfide structure the SH peak at 3.7-3.9 μ was absent; in the N-arylaminomethyl aryl sulfides a sharp spike occurred at 2.9 μ, characteristic of the NH stretching in secondary amines; at 8 μ the peak showed aromatic amines; a band at 7.4-7.6 and a triplet at 8.1-8.5 μ were characteristic of tertiary amines; a triplet at 10 μ was also characteristic of the tertiary amines; spectra of 2,4,6-trimethylphenylaminomethyl 2,4,6-trimethylphenyl sulfide indicated a definite existence of steric hindrance. Potentiometric titrations of I (Ar1 = Ph, Ph, Ph, Ph, and Ar2 = Ph, p-ClC6H4, 2,4,6-Me3C6H2, C6Cl5) with HClO4 in AcOH gave end points at acid vols. that represented neutralization equivs. approx. double the formula wt. When the neutralization equiv. of the 2nd compd. was detd. by conductiometric titration using the same HClO4 in AcOH the equiv. was equal to the formula wt. Placing a MeO or Me group p- or Me groups in the 2, 4, or 6-positions to the amine in I apparently increased the basicity. When a Cl atom was o, m, or p to the amine group the condensation product was neutral towards HClO4 in AcOH. A p-NO2 group also produced a neutral compd. Cl was not only o-p directing but also deactivated the ring. It was thought that steric effects played an important role in the case of the compd. prepd. from thiomesitol and mesidine. The o-Me groups on the amine and thiol nucleus made it more difficult for the protonating agent to attack the N atom. The 1,3,5-triaryl-1,5-dithia-3-azapentanes were neutral when titrated with HClO4 in AcOH. The electron withdrawal of the 2 thiomethyl and an aryl group reduced the basicity of the N atom so that the tertiary amine was neutral.

ACCESSION NUMBER: 1960:28452 CAPLUS
DOCUMENT NUMBER: 54:28452
ORIGINAL REFERENCE NO.: 54:5530i,5531a-i,5532a-c
TITLE: Condensation of thiophenols and formaldehyde with some aromatic amines
AUTHOR(S): Grillot, Gerald F.; Schaffrath, Robert E.
CORPORATE SOURCE: Syracuse Univ., Syracuse, NY
SOURCE: Journal of Organic Chemistry (1959) 1035-8
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB cf. C.A. 52, 284c. Tertiary amines containing aromatic groups are brominated
in the nucleus; with ease and in good yields by N-bromosuccinimide (I); aromatic amines are substituted under these conditions exclusively in the p-position. Amines of this type undergo with Pb(OAc)4 (II) in Ac2O oxidative dealkylation. (PhCH2)3N (28.7 g.) in 150 cc. dry C6H6 treated at 20-30° with stirring with 18 g. I in portions, the mixture heated 0.5 hr. at 80°, poured into iced H2O, and filtered gave 25 g. (PhCH2)2NH.HBr, m. 246-8°; the C6H6 layer yielded 10 g. BzH. iso-PrMeNPh (14.9 g.) in 80 cc. dry C6H6 and 18 g. I allowed to stand 5 min., filtered, evaporated, and distilled yielded 14 g. p-BrC6H4NMeCHMe2, b2 105°, m. 32-4°. A series of similar runs were performed with the following amines (products and % yield given): Et3N, AcH and Et2NH, - (1 hr. reaction time); Ph3N, p-BrC6H4NPh2, 50 (3 hrs. reaction time); 1-C10H7NHMe (III), 4-Br derivative of III, 70; 2-C10H7NH2 (IV), 1-Br derivative of IV, -; PhNEt2 (V), p-Br derivative of V, -; PhMeNCH2Ph, p-BrC6H4NMeCH2Ph, 85 (5 min. reaction time); (PhCH2)2NPh, p-BrC6H4N(CH2Ph)2, 82. p-O2NC6H4NMe2 and PhNMe2.EtBr did not react under these conditions. PhNMe2 (6 g.) in 25 cc. CHCl3 and 10 cc. Ac2O treated dropwise under N during 30-40 min. with 22.15 g. II in 50 cc. CHCl3, the mixture stirred 1 hr. with occasional cooling and filtered, the CHCl3 layer washed with 200 cc. H2O, the combined aqueous solns. treated with 50 cc. 2N H2SO4, filtered, and the filtrate treated with 2,4-(O2N)2C6H3NHNH2 gave 61% CH2O derivative; the CHCl3 layer evaporated in vacuo gave 6.1 g. MePhNAc, m.
102°. Similar dealkylations with II were performed using the following tertiary amines (% yields of aldehyde and N-Ac derivative of the secondary amine, product, and m.p. of product given): PhNEt2, 93, 90, EtPhNAc, 51°; p-MeC6H4NMe2, 91, 87, p-MeC6H4NAcMe, 82°; p-MeOC6H4NMe2, 80, 82, p-MeOC6H4NAcMe, 78° (resin formation); p-ClC6H4NMe2, 66, 56, p-ClC6H4NAcMe, 91°; p-O2NC6H4NMe2, 51, 82, p-O2NC6H4AcMe, 151°; 2-C10H7NMe2, 27, 22, 2-C10H7NAcMe, 50° (strong resinification); p-Me2NC6H4CHO, 50, 44, p-OHCC6H4NAcMe, 56°; (p-Me2NC6H4)2CO (VI), 71, 90, p-AcMeNC6H4COC6H4NMe2-p, 137°. VI, 2 mole equivs. II, 50 cc. CHCl3, and 20 cc. Ac2O yielded similarly 35% (p-AcMeNC6H4)2CO, m. 92°.

ACCESSION NUMBER: 1959:62378 CAPLUS
DOCUMENT NUMBER: 53:62378
ORIGINAL REFERENCE NO.: 53:11277g-i,11278a-c
TITLE: The course of substitution. XIV. The reaction of tertiary amines with N-bromosuccinimide and lead tetraacetate
AUTHOR(S): Horner, Leopold; Winkelmann, Erhard; Knapp, Karl H.; Ludwig, Werner
CORPORATE SOURCE: Univ. Mainz, Germany
SOURCE: Chemische Berichte (1959), 92, 288-92
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LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 53:62378

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AB Abietic acid (I) was condensed with HCHO (II) in EtCO2H (III) solution to give 51% 8,9-bis(methylenepropionoxy)abietic acid (IV), isolated as the cyclohexylamine salt (V). Hydrolysis of V afforded 8,9-dimethylolabietic acid (VI). The structure of VI was established by catalytic dehydrogenation to 1,8,10-trimethyl-2-isopropylphenanthrene (VII) and comparison with the totally synthesized compound All attempts to cause I to react with II in aqueous solution or in inert solvents such as diisopropyl ether or p-dioxane failed; I could be recovered unchanged in each case. Similarly attempts to condense I with HCHO in the presence of 10% H2SO4 gave unchanged material. Aqueous NaH2PO4 used in excess was found to be a good reagent for the regeneration of I from its amine salt. Purified I showed [α]25D -101.6°. I (10g.) and 1 g. HCHO suspended in 50 ml. dioxane, 3 g. concentrated H2SO4 added and the temperature
kept 0.5 hr. at 60°, 300 ml. H2O added, and the precipitate collected and dried gave a product which could not be crystallized Expts. similar to the above were run using 2, 3, and 5 moles II/mole I. These products showed neutralization equivs. of 357, 394, and 419, resp., but a crystalline product
could not be obtained. The product from the condensation of I with 2 moles II showed no maximum in the 220-285 mμ region. Use of H3PO4 and BF3.Et2O gave similar results. I (10 g.) in 50 ml. dioxane was treated with 1 g. concentrated H2SO4, 10 ml. aliquots drawn at intervals and the content
of I estimated from the absorption at 241 mμ. I (3 g., [α]25D -101.6°) in AcOH refluxed 18 hrs. gave 2.7 g. I, [α]25D -100.4°. I (10 g.), 2.2 g. II, and 50 ml. AcOH refluxed 18 hrs., the AcOH distilled, and the residue taken up in Et2O gave a glass which could not be crystallized Aliquots of a solution of 20 g. of the condensation product in 40 ml. Me2CO were treated at reflux with an equivalent
amount of the following amines: Pr2, iso-Pr2, Bu, sec-Bu, iso-Bu, Bu2, iso-Bu2, 1-amino-2-hydroxypropane, 2-amino-1-hydroxy-2-methylpropane, Am, iso-Am, Am2, PhCH2, N-methylbenzyl, cyclohexyl, and piperidine. Cyclohexylamine produced a crystalline salt (VIII) after 1 min., whereas the other amines failed to crystallize after 30 days at 7°. This salt on purification m. 185°, λ 251.5 mμ, ν 5.76 and 6.40 μ. VIII (5 g.) suspended in 100 ml. Et2O shaken with 20 g. NaH2PO4 in 100 ml. H2O, the Et2O layer separated, washed, dried, and concentrated gave 95% 8,9-bis(methyleneacetoxy)abietic acid (IX), m.
73-5° (sealed capillary) (C7H16), λ 251.5 mμ, ν 5.76 and 5.88 μ. IX (25 g.) refluxed 2.5 hrs. with 15 g. KOH in 70 ml. H2O and 70 ml. alc., the cooled solution shaken with 300 ml. Et2O and 20 g. NaH2PO4 in 300 ml. H2O, the Et2O layer washed, dried, and distilled and the amorphous solid crystallized gave 11.5 g. VI, m. 192-3° (alc.), λ 251.5 mμ, ε 24,200, [α]25D 143.2°. I
(150 g.), 33 g. II, and 750 ml. III refluxed 20 hrs., excess III removed, and the residue taken up in Et2O, washed, dried, and distilled gave a yellow glass which could not be crystallized This crude IV was dissolved in
350 ml. Me2CO and refluxed with 100 g. cyclohexylamine, left at 7° overnight, the crude salt collected, and recrystd. to give 145 g. V, m. 175° (ligroine), [α]25D 85.6°, λ 251.5 mμ. IV was liberated from V and subsequent basic hydrolysis as described above gave VI identical with the above prepared specimen. Treatment of VI with tosyl chloride in C5H5N gave a yellow solid showing infrared spectrum bands at 5.75 and 5.88 μ. There also appeared to be OH absorption at 3.0 μ. VI (32 g.) treated with CH2N2 and then

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dissolved in 200 ml. C5H5N and treated 2.5 hrs. at 0° with 33.5 g. tosyl chloride, 30 ml. H2O added portionwise during 0.5 hr., the suspension poured into 200 ml. H2O, extd. with CHCl3, the exts. washed, dried, and distd. gave 44 g. of the ditosylate (X) of the Me ester of VI, ν 7.28, 8.40, 8.48, 10.45, and 14.28 μ, all attributed to the tosylate functions. X (40 g.) in Et2O added dropwise to 7.5 g. LiAlH4 and 200 ml. Et2O, refluxed 1 hr., decompd. with EtOAc, the mixt. treated with NH4Cl, and distd. gave 23 g. of a product which showed infrared bands characteristic of the tosylate function; reduction of the carbomethoxy group to methylol appeared to be complete. This material dissolved in 200 ml. Bu2O added to 7 g. LiAlH4 in 100 ml. Et2O, the mixt. refluxed 3 hrs., and worked up as above gave 16 g. of a product which gave no bands for the tosylate function, but there was some absorption in the carbonyl region and fairly strong bands at 8.50 and 8.74 μ. This substance may be a mixt. of 8,9-dimethylabietinol and the cyclic ether. This mixt. (10.5 g.) treated with tosyl chloride gave a tosyl deriv. which was reduced with LiAlH4 in Bu2O to give 6.2 g. yellow oil, which showed no OH absorption but still showed strong absorption at 8.50 and 9.74 μ indicating the presence of the ether function. Dehydrogenation of 2 g. VI over 2 g. 10% Pd-C 4 hrs. at 300-30° gave 0.2 g. of the trinitrobenzene complex of retene, m. 143-4°. No other product was isolated. VI (10 g.) in 100 ml. MeOH catalytically reduced 24 hrs. at 50 lb./sq. in. over 2 g. 10% Pd-C and worked up gave a solid which could not be recrystd. from the common solvents; it had no ultraviolet absorption in the 220-85 mμ region. 8,9-Dimethyloltetrahydroabietic acid (4 g.) dehydrogenated 4.25 hrs. at 300-30° under CO2 over 2 g. 10% Pd-C, cooled, extd. with Et2O, filtered, and evapd. gave a residue, treated with picric acid to give 2.2 g. VII picrate, m. 177-8° (alc.). The picrate in 100 ml. Et2O shaken with 2 50 ml.-portions 10% Na2CO3 gave 0.83 g. VII, m. 84-5° (MeOH). Na (31 g.) in 600 ml. alc. treated with 238 g. MeCH(CO2Et)2, then 260 g. o-bromo-o-xylene added dropwise so as to maintain reflux, the mixt. refluxed 4 hrs. longer, decompd., the crude ester refluxed 8 hrs. in 200 ml. H2O with 200 g. KOH, the clear soln. washed with Et2O, treated with 500 ml. 10N H2SO4, refluxed 5 hrs., the org. layer sepd., and the exts. combined, washed, dried, and distd. gave 152 g. α-methyl-β(o-tolyl)propionic acid (XI), b3 147-50°; amide, m. 109-10°. XI (152 g.), 120 g. alc., 300 ml. C6H6, and 3 ml. concd. H2SO4, refluxed 8 hrs. under a Dean and Stark H2O trap, and distd. gave 156 g. XI Et ester (XII), b1.5 97-9°. XII (156 g.) in 350 ml. Et2O added dropwise during 1 hr. to 28 g. LiAlH4 and 800 ml. Et2O, decompd. with EtOAc, then with 10% HCl gave 118 g. 2-methyl-3-(o-tolyl)-1-hydroxypropane (XIII), b1.5 101-2°. XIII (110 g.) and 200 g. C5H5N treated dropwise between 0-5° with 85 g. PBr3, stirred 0.5 hr. at 5°, 200 ml. Et2O added, the stirring continued 1 hr. at 5°, left at room temp. overnight, H2O added, extd. with Et2O, and the exts. washed with 100 ml. 10% HCl, then with H2O, dried, and distd. gave 114 g. 1-bromo-2-methyl-3-(o-tolyl)propane (XIV), b1 95-6°. XIV refluxed 40 hrs. with 38 g. KCN in 150 ml. H2O and 50 ml. alc., cooled, dild. with 400 ml. H2O, the org. layer sepd., refluxed with 70 g. KOH in 140 ml. H2O, cooled, treated with 70 g. concd. H2SO4 in 200 ml. H2O, extd. with Et2O, and distd. gave 60 g. β-methyl-γ-(o-tolyl)butyric acid (XV), b1.5 151-3°; p-toluidide, m. 107-8°. XI (100 g.) and 140 g. SOCl2 left overnight gave after a 1-hr. reflux 102 g. α-methyl-β-(o-tolyl)propionyl chloride (XVI), b9 120-1°. XVI (100 g.) in 250 ml. Et2O left 15 min. at 5-10° with CH2N2 in Et2O, left at room temp. overnight, the Et2O removed, the crude product dissolved in 500 ml. dioxane, treated 1

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hr. at 60° with 10 g. Ag2O, 25 g. Na2CO3, and 1.5 g. Na2S2O3 in 1 l. H2O, refluxed 2 min., cooled, treated with 25 g. Na2CO3, extd. with Et2O, and the ext. distd. gave 49.6g. XV. XV (45 g.) and 100 g. SOCl2 left overnight at room temp. and refluxed 1 hr. gave 46 g. β-methyl-γ-(o-tolyl)butyryl chloride (XVII), b7.5 131-2°. XVII (38.7 g.) in 40 ml. ligroine added to 35 g. AlCl3 and after the initial reaction, the system refluxed 2 hrs., the complex decompd. by addn. of 10% HCl at 5°, the org. layer sepd., and distd. gave 24 g. 3,5-dimethyl-1-tetrahydronaphthalenone (XIX), b1.5 118-20°, m. 63-4°. XIX (22 g.) and 22 g. BrCH2CO2Et in 50 ml. each C6H6 and PhMe treated with 9 g. Zn and a crystal of iodine, after the reaction began the remainder of the soln. added, an addnl. 9 g. Zn and 10 g. BrCH2CO2Et added, and refluxing continued 3 hrs., cold. dil. HCl added, and the org. layer extd. with C6H6 gave 5.3 g. unreacted XIX and 14.2 g. Et 1-(3,5-dimethyl-3,4-dihydronaphthyl)acetate (XX), b3 156-8°. XX (2.16 g.), 1.90 g. N-bromosuccinimide, and 20 ml. CHCl3 refluxed 3 hrs., the system cooled, filtered, and distd. gave a residue which heated 2 hrs. in vacuo on the H2O bath gave a material showing no CO absorption in the infrared, m. 46-9°; picrate, m. 140-1°. XX (14 g.) in 150 ml. MeOH acidified with 2 drops concd. HCl and hydrogenated 12 hrs. at 25° and 50 lb./sq. in. with 10% Pd-C gave 10.5 g. Et 1-(3,5-dimethyl-1,2,3,4-tetrahydronaphthyl)acetate (XXI), b2 142-3°. XXI (11 g.) dehydrogenated 9 hrs. under N at 320° over 1 g. 10% Pd-C with evolution of 2100 ml. H gave 8.9 g. Et 1-(3,5-dimethylnaphthyl)acetate (XXII), b2 156-8°. XXII (8.9 g.) in 30 ml. Et2O added dropwise to 5 g. LiAlH4 in 50 ml. Et2O, excess LiAlH4 destroyed, dil. HCl added and the Et2O phase sepd., and washed gave the crude alc. This alc. treated at 5-10° with 5.5 g. PBr3 and left 4 hrs. at room temp. gave 8.6 g. 1-bromo-2-(3,5-dimethyl-1-naphthyl)ethane (XXIII), b8 173-5°. XXIII (26 g.) added slowly to a refluxing soln. of the Na salt of iso-PrCH(CO2Et)2 (from 2.4 g. Na, 21 g. iso-PrCH(CO2Et)2 and 4.8 g. alc. in 60 ml. PhMe), the mixt. refluxed 12 hrs., the PhMe removed, the residual oil taken up in Et2O, washed, evapd., and the residue refluxed 8 hrs. with 20 g. KOH and 20 ml. H2O, cooled, treated with 15 ml. H2O, extd. with C6H6, and the clear soln. treated cautiously with 50 ml. 10N H2SO4, refluxed 6 hrs., and extd. gave 8.3 g. α-isopropyl-γ-(3,5-dimethyl-1-naphthyl)butyric acid (XXIV), b1.5 225-7°. XXIV (4.5 g.) in 20 ml. C6H6 left 1 hr. at room temp. with 4.3 g. PCl5, heated 5 min. on the H2O bath, cooled to 5°, 4.5 ml. SnCl4 added, the system left 15 min. at 5°, decompd. with acid, the org. phase sepd., and the C6H6 evapd. gave 3.2 g. 8,10-dimethyl-2-isopropyl-1-oxo-1,2,3,4-tetrahydrophenanthrene (XXV), m. 56-8° (MeOH). XXV (3 g.) in 15 ml. Et2O added at 5° to MeMgI (from 7 g. MeI) in Et2O, left overnight, poured into cold dil. HCl, the Et2O layer sepd. and the Et2O evapd. gave a residue which dehydrogenated by heating 1.5 hrs. at 310° over 1 g. 10% Pd-C under N, the system cooled, the product taken up in Et2O, and the solvent evapd. gave 2.6 g. VII, m. 85-6°; picrate, m. 175-6°. A mixt. of this synthetic VII was identical with the product isolated from dehydrogenation of the abietic acid deriv. The mixed m.p. of the picrates was 175-7°.

ACCESSION NUMBER: 1959:34684 CAPLUS
DOCUMENT NUMBER: 53:34684
ORIGINAL REFERENCE NO.: 53:6177d-i,6178a-i,6179a-f
TITLE: Condensation of abietic acid with formaldehyde
AUTHOR(S): Royals, E. Earl; Greene, Joseph L., Jr.
CORPORATE SOURCE: Emory Univ.,Emory Univ., GA
SOURCE: Journal of Organic Chemistry (1958), 23, 1437-43
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal

L7 ANSWER 29 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 53:34684

L7 ANSWER 30 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

AB cf. C.A. 51, 11354i. Et2NCH2OBu (I), b18 71-2°, and styrene were made to react in 2:1 mole ratio by blowing in BF3 below 10° until approx. 2 moles BF3 is absorbed, stirred 30 hrs. at room temperature, extracted with Et2O, and distilled to give a joint compound, Et2N(CH2)2CHPhOBu, b7.5 89-90°, HCl salt, m. 151-2°. Similarly, 64 g. I and 10 g. ethylene oxide in the presence of 40 g. BF3 gave 4 g. Et2NCH2O(CH2)2OBu, b6 76.5-7.0°, and 2 g. Et2NCH2O(CH2)2O(CH2)2Bu, b6 116°. R2NCH2OR' (II) was treated with ketene by blowing in the latter with cooling in the presence of ZnCl2, extracting, and distilling to give the corresponding 2 joint compds.: the low-boiling compound was a β-aminopropionic ester and the high-boiling, an amide (R and R' of II, b.p. or m.p. of both products, and % yields given): Et, Et, b11.5 75-6°, 9.72%, b6 103-6°, 35.2%; Et, Bu, b8 93.5-4.5°, 9.95, b6103-5° 20.0; [R2 = O(CH2-CH2)2], Bu, b10 117-18°, 14.0, m. 89-93°, 3.5; [R2 = (CH2)5], Bu, b5.5 101-2°, 18.8, m. 37-41°, 53.6. R2NCH2NR2 gave similarly the joint compds. with ketene (R, b.p. and % yield given): Et, b6 103-6°, 40.0; [R2 = O(CH2CH2)2], b7.5 187-9°, 57.9; [R2 = (CH2)5], b7 148-55°, 77.4. Joint compound of benzoic amide and NaHSO3 with HCHO (PhCONHCH2SO3Na) (7 g.) was treated with 18 g. PhCONH2 in the presence of EtONa at 190-200° to give 84% PhCONHCH2NHCOPh, m. 219.0-19.5°. Similar reactions with phthalimide gave 51% PhCONHCH2N(CO)2C6H4-o, m. 183-4°, and with carbazole, 49% PhCONHCH2N(C6H4)2, m. 199.0-9.5°.

ACCESSION NUMBER: 1959:29086 CAPLUS
DOCUMENT NUMBER: 53:29086
ORIGINAL REFERENCE NO.: 53:5262b-e
TITLE: Joint reaction and trans jointing
AUTHOR(S): Oda, Ryohei; Tanimoto, Shigeo; Nomura, Motoaki; Nishimura, Tsunehiko; Kyo, Kayomon
CORPORATE SOURCE: Kyoto Univ.
SOURCE: Kogyo Kagaku Zasshi (1957), 60, 18-20
CODEN: KGKZA7; ISSN: 0368-5462
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 31 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN

GI For diagram(s), see printed CA Issue.

AB A solution of 40% NaHSO3 (1 mole) ice-cooled, 40% CH2O added, the mixture stirred 2 hrs., warmed at 25-30°, 1 mole MeNH2 added, stirring continued 2 hrs., 1 mole KCN added, the mixture stirred 2 hrs., then extracted with Et2O, and the extract distilled gave 54% MeNHCH2CN (I), b29 70°, n35D 1.4081. Similarly, other RNHCH2CN (II) were prepared (R, b.p./ mm., nD/t°, and yield shown): Et, 81°/29, 1.4370/35°, 56; Pr, 91°/20, 1.4370/35°, 65; iso-Pr, 80°/29, 1.4179/23°, 70; and Bu, 105°/29, 1.4226/36°, 66. Reduction of the II with LiAlH4 gave the compds. RNH(CH2)2NH2 (R, b.p., nD/t°, and % yield shown): Me, 115-16°, 1.4391/24°, 54; Et, 128-9°, 1.4396/24°, 61; Pr, 147-50°, 1.4331/31°, 55; iso-Pr, 136-7°, 1.4420/19°, 74; and Bu, 169-72°, 1.4368/30°, 65. EtNH(CH2)2NH2 (3.3 g.) in 50 ml. CHCl3 with 10.35 g. K2CO3 treated dropwise with 3.97 g. AcCl in 15 ml. CHCl3 with ice cooling, and the mixture stirred 1 hr. gave 4.0 g. AcEtN(CH2)2NHAc, b3 180°, n29D 1.4711. Similarly, MeNH(CH2)2NH2 with Et2NCOCl gave 60% Et2NAcN(CH2)2NHCONEt2, b3 202°, n26D 1.4796. HCHO (35% weight/volume) added to a cooled solution of RNH(CH2)2NH2 in C6H6, the mixture heated from 80° to 100°, and the H2O distilled gave the compds. (R, b.p./mm., nD/t°, and % yield shown): Me, 113°/8, 1.4788/24°, 67; Et, 130°/8, 1.4716/35°, 80; Pr, 149°/8, 1.4681/32°, 62; and Bu, 160°/3, 1.4693/30°, 60. iso-PrNH(CH2)2NH2 (III) (4.05 g.) in 100 ml. C6H6 treated with 2.85 g. PrCHO, stirred 5 hrs., and distilled gave 4.6 g. 1-isopropyl-2-propylimidazoline (IV), b100 121°, n32D 1.4540. EtO2CCl (4.25 g.) in 20 ml. alc. added to 3.05 g. IV, 4.15 g. Na2CO3, and 150 ml. alc. at reflux, the mixture stirred 5 hrs., cooled, filtered, the filtrate evaporated, and the residue dissolved in 30 ml. 5% NaOH and extracted with Et2O gave EtO2C (iso-Pr)N(CH2)2NHCO2Et, b5 160°, n35D 1.4449. A solution of 5.1 g. III in 50 ml. Et2O cooled, 4.2 g. CS2 added dropwise, the mixture stirred 1 hr., and the precipitate filtered, dried, and heated 2 hrs. at 130-40° gave 5.2 g. 1-isopropyl-2-imidazolidinethione (V), m. 166°. V in PhMe with excess PhNCO at reflux 12 hrs. gave 90% 1-isopropyl-3-phenylcarbamoyl-2-imidazolidinethione, m. 104-5°. Similarly, 1-ethyl-3-phenylcarbamoyl-2-imidazolidinethione, m. 83-4°, and the 1-Bu homolog, m. 68-9°, were prepared 1-Ethyl-2-imidazoli-dinethione (1 g.) and 1.5 g. Et2NCOCl heated 2 hrs. on a steam bath and 2 hrs. at 130°, and the mixture evaporated, treated with 5% NaOH, and extracted with C6H6 gave 1-ethyl-3-diethylcarbamoyl-2-imidazolidinethione.

ACCESSION NUMBER: 1958:88121 CAPLUS
DOCUMENT NUMBER: 52:88121
ORIGINAL REFERENCE NO.: 52:15549d-i
TITLE: Studies in potential filaricides. II. Synthesis of substituted imidazolidines and 2-imidazolidinethiones
AUTHOR(S): Wadia, P. S.; Anand, Nitya; Dhar, M. L.
CORPORATE SOURCE: Central Drug Research Inst., Lucknow
SOURCE: Journal of Scientific & Industrial Research (1958), 17B, 24-30
CODEN: JSIRAC; ISSN: 0022-4456
DOCUMENT TYPE: Journal
LANGUAGE: English

L7 ANSWER 32 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB Condensation products are obtained when an amide reacts with HCHO and a hexitylamine (produced by reduction of the corresponding hexosamine). Thus, 493 g. N-methylglucamine (I) (produced by the simultaneous reaction of glucose, H, and MeNH2) and 505 g. of lauramide were dissolved in 1750 mL. MeOH and 75 g. paraformaldehyde was added. The mixture was heated for 2 h. under reflux and the MeOH and the water of reaction were removed by distillation, first at atmospheric pressure and finally under a vacuum of 1-2 mm. at a maximum temperature of 125°. A firm, waxy condensation product remained in the pot. Other amides which were treated with I and HCHO were melamine, stearamide, oleamide, urea, phthalimide, and acetamide. The products are said to be useful as surfactants, antistatic and textile-finishing agents, corrosion inhibitors, lubricants, additives, waxes, and resins.

ACCESSION NUMBER: 1958:13648 CAPLUS
DOCUMENT NUMBER: 52:13648
ORIGINAL REFERENCE NO.: 52:2457a-c
TITLE: Amide condensation products
INVENTOR(S): Zech, John D.
PATENT ASSIGNEE(S): Atlas Powder Co.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2813091		19571112	US	

L7 ANSWER 33 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB cf. C.A. 51, 6528c. The β-sulfoethylations with Na isethionate of N-methyloleylamide, N,N'-distearoylethylenediamine*, ** , 2-heptadecylindole, and 2-heptadecylbenzimidazole were conducted. The amount (g.) and name of starting compound, amount (g.) of Na isethionate, reaction temperature, reaction time, and yield (%) of purified product were: 10, ***N-methyloleylamide, 10, 220°, 13, 20; 8, N,N'-distearoylethylenediamine, 13, 210°, 11, 17; 3, 2-heptadecylindole, 3, 210°, 12, 33; 10, 2-heptadecylbenzimidazole, 8, 220°, 9, 30. As catalyst 0.3 g. powdered NaOH was used in every case and the products were recrystd. from alc. or water. Et orthoformate (50 g.) and 30 g. acetamide refluxed 15 hrs., cooled, filtered, and washed with acetone gave 23-27.7% MeCONHCH:NCOMe which showed no distinct m.p. after 3 recrystns. Similarly, 27 g. Et orthoformate and 12 g. benzamide gave 9.2 g. PhCONHCH:NCOPh, m. 297-8°. N-methylolphthalimide and benzoic acid, both 0.1 mole, in 100 cc. 95% H2SO4 left 4 days at 10-15°, poured into water, the precipitate filtered off, extracted with NaOH solution, and acidified with HCl gave 17 g. m-phthalimidomethylbenzoic acid (I), m. 228.5-30.5° (from alc.). I was hydrolyzed by refluxing in 20% NaOH, acidified with HCl, filtered to remove phthalic acid, and the filtrate evaporated to dryness to give 88.5% m-aminomethylbenzoic acid hydrochloride, m. 250-1°; treatment with Amberlite IR-4B gave the free amine, m. 246-8°. Heating the free amine at 245-55° 5 hrs. gave a brittle and hard resin. Quinaldine (50 g.), 25 cc. water, 27 cc. EtOH, and 1.5 equivalent HCHO (37% solution) was refluxed 24 hrs., the solvent distilled, and the residual 2-hydroxyethylquinoline dehydrated to 7% 2-vinylquinoline (II) by distilling with 1.3 g. NaOH and 0.5 g. N-phenyl-β-naphthylamine. The β-(2-quinolino)ethylations were successfully conducted from II with PhCOMe, PhCOEt, and CH2(CO2Et)2. Vinyl Bu ether was heated 10 hrs. in the presence of p-toluenesulfonic acid as a catalyser with dialkylaminomethyl Bu ethers from piperidine, Et2NH, and morpholine to give 72% C5H10NCH2CH2CH(OBu)2, b5.5 154-5°, 60% Et2N(CH2)2(OBu)2, b4.5 122-3°, and 77% CH2.CH2.O.CH2.CH2.NCH2CH2CH(OBu)2, b5 155-7°, resp. Hydrolysis of these aminoaldehyde acetals with HCl gave free aldehydes which readily polymerized. β-Piperidinopropionaldehyde di-Bu acetal in ether was treated with dry HCl and the precipitate collected quickly to give the free aldehyde hydrochloride, m. 133-6°. The 2,4-dinitrophenylhydrazone of this aminoaldehyde was obtained from the di-Bu acetal. That the last 3 reactions are transjointing has been shown. Another transjointing reaction with benzyl β-sulfoethyl ether was described. Benzyl β-sulfoethyl ether was prepared (70%) by adding 1.5 g. powdered NaOH to a refluxing mixture of 150 g. benzyl alc. and 45 g. Na isethionate and keeping at 180° 7 hrs. The transjointing reaction with malonic ester was conducted by adding 100 g. di-Et malonate to 50 cc. absolute alc. containing 1.3 g. Na, removing the solvent, adding 11 g. benzyl β-sulfoethyl ether, heating 20 hrs. at 170°, washing with ether, dissolving the residue in water, and acidifying; yield 25%. Similarly, transjointings with acetoacetic ester and aniline were performed in 20 and 22% yields, resp.

ACCESSION NUMBER: 1957:62378 CAPLUS
DOCUMENT NUMBER: 51:62378
ORIGINAL REFERENCE NO.: 51:11355b-i
TITLE: Joint reaction and transjointing. III
AUTHOR(S): Oda, Ryohei; Teramura, Kazuhiro; Tanimoto, Shigeo;

L7 ANSWER 33 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
Nomura, Motoaki; Suda, Hideaki; Matsuda, Kazuo
CORPORATE SOURCE: Kyoto Univ.
SOURCE: Bulletin of the Institute for Chemical Research, Kyoto University (1955), 33, 117-25
CODEN: BICRAS; ISSN: 0023-6071
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 34 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB cf. C.A. 50, 921i. HC(OEt)3 (27 g.) and 12.0 g. BzNH2 refluxed 12 hrs., cooled, and the solid washed with water and then with hot water yielded 8.2 g. BzNHCH:NBz, m. 297-8°. Similarly 50 g. HC(OEt)3 and 30 g. AcNH2 gave 27% AcNHCH:NAc, which readily decomposed CH2(NHBz)2 (50 g.) and 25 g. CH2(NHAc)2 heated gradually up to 270° and refluxed 9 hrs., the product added to 250 cc. water, extracted with ether and CHCl3, and the insol. residue recrystd. from water repeatedly gave 2.0 g. BzNHCH2NHAc, m. 179.5-81°. Transjointing between 11.5 g. 1,3-diphenylimidazolidine and 16.0 g. CH2(CO2Et)2 with 2 g. CaCl2 or ZnCl2 as catalyst in EtOH produced 95% (PhNHCH2)2 and 53% (CH2)3(CO2H)2 (after decarboxylation). Similarly PhNMe2 and 1,3-diphenylimidazolidine gave (p-Me2NC6H4)2CH2 and β-naphthol and 1,3-diphenylimidazolidine gave 65% α,α'-methylenebis-β-naphthol. Refluxing 6 hrs. 38 g. CH2(OCH2Ph)2, 23 g. CH2(OEt)2, and 3 g. ZnCl2, treating the mixture with excess aqueous NaHCO3, extracting with benzene, drying, and repeatedly distilling the benzene layer gave 8.9 g. EtOCH2OCH2Ph, b24 105-11°. NaOEt from 3 g. Na, 16.5 g. BuOCH2CH2CN, and 9.5 g. Et2NH were warmed at 40-50° 4 hrs., left overnight at room temperature, heated at 75° for a while, and neutralized with AcOH to give after fractionation by distillation 6.7 g. Et2NCH2CH2CN, b35 102°. Similarly 25.4 g. BuOCH2CH2CN, 32 g. CH2(CO2Et)2, and 4.6 g. Na gave 16 g. NCCH2CHCH(CO2Et)2, b5 145-51°. NCCH2CH2NEt2MeI (14 g.) and 43.5 g. morpholine heated 3 hrs. at 110° and distilled gave 3.5 g. β-morpholinopropionitrile, b13 130-3°; NCCH2CH2CH(CO2Et)2 was similarly obtained. PhBr (30 g.) was converted into PhMgBr, 15 g. CH2(NEt)2 added, and the mixture refluxed 4 hrs. From the reaction product, 4 g. PhCH2NEt2, b15 87°, was obtained; no Ph2CH2 was detected even when excess Grignard reagent was used. Similarly PhCH2MgCl (from 20 g. PhCH2Cl) and 25 g. CH2(NEt)2 produced 15.3% PhCH2CH2NEt2. The Grignard reagent from 31.4 g. PhBr added slowly to 16 g. Et2NCH2OBu gave 11.5 g. PhCH2NEt2, b15 90.5-91°. PhCH2CH2NEt2 was also produced similarly in 91% yield. Et2NCH2OBu (29 g.) and 5.4 g. urea heated 20 min. and distilled gave 20 g. residue from which (Et2NCH2NH)2CO was identified as picrate.

ACCESSION NUMBER: 1956:36075 CAPLUS
DOCUMENT NUMBER: 50:36075
ORIGINAL REFERENCE NO.: 50:7112b-g
TITLE: Joint reaction and transjointing. II
AUTHOR(S): Oda, Ryohei; Nomura, Motoaki; Tanimoto, Shigeo
CORPORATE SOURCE: Kyoto Univ.
SOURCE: Bulletin of the Institute for Chemical Research, Kyoto University (1954), 32, 231-7
CODEN: BICRAS; ISSN: 0023-6071
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 35 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB New syntheses of 3-aryl-3-butenylamines, substituted cinnamylamines, and 1-aryl-3-aminopropanols by the reaction of substituted styrenes, CH2O, and secondary amines in AcOH are reported. Unsatd. tertiary amines have been obtained from the reaction of several terpenes, CH2O, and secondary amines. The appropriate amine (1 mole) in 400 cc. AcOH treated with 31.6 g. paraformaldehyde, the mixture heated until a clear solution was obtained, the solution treated with 1 mole of the appropriate amine , the mixture refluxed with stirring, poured into H2O, and extracted with C6H6, the aqueous layer basified with excess NaOH and extracted with C6H6, and the extract dried and distilled gave the corresponding 3-aryl-3-butenylamine. In this manner were prepared the following compds. PhC(:CH2)(CH2)2X (X, b.p./mm., nD25, reaction time in hrs., and % yield given): Me2N (I), 65-70°/0.5, 1.5225, 16, 60 [(Me2N)2CH2 was used as the source of the amine and 50% of the required CH2O]; Et2N (II), 145-6°/25, 1.5126, 5, 33; morpholino (III), 175-80°/15, 1.5439, 16, 30; NMeCH2Ph, 140-50°/1, 1.5615, 16, 39; the p-Me derivs. of I (IV), 115-20°/6, 1.5209, 6, 56; of II, 110-15°/2, 1.5156, 16, 34; of III, 160-5°/4, 1.5407, 16, 51; piperidino analog of IV, 145-8°/4, 1.5363, 16, 32; pyrrolidino analog of IV, 125-30°/2, 1.5384, 16, 18. Similar condensations with CH2O were carried out with the following terpenes and secondary amines (b.p./mm., nD25, and % yield of the condensation product, and reaction time in hrs. given): α-pinene, Me2NH, 120-30°/18, 1.4819, 33, 30; β-pinene, Me2NH, 133-43°/20, 1.4771, 65, 2; camphene, Me2NH, 55-65°/0.3, 1.4789, 21 (26% with Me2NH.H2SO4), 16; d-limonene, Me2NH, 70-80°/0.3, 1.4809, 24, 16; dipentene, piperidine, 105-14°/0.75, 1.5000, 22, 16; β-pinene, piperidine, 115-25°/2, 1.4977, 28, 16; camphene, morpholine, 87-97°/0.6, 1.5025, 24, 16; β-pinene, morpholine, 170-80°/10, 1.4985, 44, 16; d-limonene, morpholine, 100-10°/0.3, 1.5030, 18, 16. In the same manner were prepared the following amino alcs. ArCH(OH)CHRCH2X (Ar, R, X, b.p./mm., nD25, % yield, and reaction time in hrs. given): p-MeOC6H4, H, morpholino, 175-85°/2.0, 1.5328, 36, 1; p-MeOC6H4, Me, Me2NH, 130-40°/1.2, 1.5144, 42, 8; 3,4-CH2O2C6H3, Me, Me2N, 125-35°/0.4, 1.5241, 34, 8. I (75 g.) in 175 cc. EtOH hydrogenated at 100° and 100 atmospheric over 7 g. Raney Ni gave 59.5 g. Me2N(CH2)2CHMePh, b20 110-13°, nD25 1.4940. p-MeOC6H4CH:CH2 (52 g.), 70 g. 76% tech. Me2NH.H2SO4 solution, 13 g. 95% paraformaldehyde, and 72 g. AcOH refluxed 18 hrs. with stirring, the mixture cooled, poured into 500 cc. H2O, and extracted with C6H6, the aqueous layer basified with excess aqueous NaOH and extracted with C6H6, and the C6H6 extract dried and distilled gave 48 g. distillate, b3 110-35°, which redistd. yielded 22 g. p-MeOC6H4CH:CHCH2NH2, b3 120-5°. Paraformaldehyde (9 g.), 120 g. AcOH, 61.5 g. Me2NH.H2SO4 heated with stirring and treated with 60 g. (p-MeOC6H4)2C:CH2, the mixture refluxed 16 hrs. with stirring, and the amine isolated in the usual manner and distilled gave 36 g. (p-MeOC6H4)2C:CHCH2NMe2, b2.2 195-205°, nD25 1.5853. HCl passed into 87.5 g. I in 216 g. PhOMe with stirring and cooling, the mixture heated to 80°, the resulting solution treated slowly with 70 g. ZnCl2, the mixture treated 1 hr. with dry HCl, heated 2 hrs. at 120°, cooled, mixed with 1 l. H2O, and 100 g. concentrated HCl, the aqueous layer basified with 500 cc. 50% aqueous NaOH and extracted with C6H6, and the C6H6 solution dried and

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distd. yielded 103 g. p-MeOC6H4CMePh(CH2)2NMe2, b4.5 185-95°, nD25 1.5564

ACCESSION NUMBER: 1956:24203 CAPLUS
DOCUMENT NUMBER: 50:24203
ORIGINAL REFERENCE NO.: 50:4964f-i,4965a-d
TITLE: The aminomethylation of olefins. I. The reaction of secondary amines, formaldehyde, and olefins
AUTHOR(S): Schmidle, Claude J.; Mansfield, Richard C.
CORPORATE SOURCE: Rohm & Haas Co., Philadelphia, PA
SOURCE: Journal of the American Chemical Society (1955), 77, 4636-8
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 50:24203

L7 ANSWER 36 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB cf. C.A. 37, 96.7. An attempt to prepare N,N-dimethylhomoveratrylamine (I) from homoveratrylamine (II) or N-methylhomoveratrylamine by the Clarke-Eschweiler reaction gave mainly 2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (III) (Clarke, et al., C.A. 28,98.9). Since the Pictet-Spengler reaction has not been observed in the absence of strong acid except with phenolic amines it seemed probable that II could be methylated with HCHO and HCO2H if acidity were avoided. Despite these precautions, the yield of I was only 44%; in addition there was a 14% yield of III and a small amount of an isomer of III. Conclusion: the Pictet-Spengler reaction (Buck, C.A. 28, 6149.3) is considerably more facile than has been previously supposed and when the structural peculiarities of a phenethylamine are favorable, the Clarke-Eschweiler reaction cannot be manipulated to avoid the cyclization completely. HCHO (10 g.) added to 9.1 g. II in a steam bath, 2.4 cc. 90% HCO2H added, the mixture heated to 87°, the pH held at about 7 by addns. of HCO2H (about 5 cc. added during 3 hrs.), 5 cc. HCHO added, 3 cc. HCO2H added in 1.5 hrs., the mixture heated 1.5 hrs. (final pH 5), the solution evaporated in vacuo, 7 cc. HCl added, the solution evaporated in vacuo, the residue dissolved in absolute EtOH and diluted with EtOAc yielded 1.7 g. III.HCl, m. 213-15° the mother liquors evaporated, the bases liberated, distilled in vacuo (below 1 mm.) yielded I; the undistd. bases (about 3 g.) yielded 0.8 g. material, C12H12NO2.HCl, m. 229-30° (decomposition) (perhaps dimethoxy-N-methyltetrahydroisoquinoline -HCl), which with permanganate gave an unidentified acid.

ACCESSION NUMBER: 1955:32414 CAPLUS
DOCUMENT NUMBER: 49:32414
ORIGINAL REFERENCE NO.: 49:6263a-d
TITLE: Competition between the Clarke-Eschweiler and Pictet-Spengler reactions
AUTHOR(S): Baltzly, Richard
CORPORATE SOURCE: Wellcome Research Labs., Tuckahoe, NY
SOURCE: Journal of the American Chemical Society (1953), 75, 6038-9
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 37 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB cf. C.A. 43, 3425e. Condensation of phenols with HCHO and primary amines yields N,N-bis(hydroxybenzyl)amines directly in certain instances. The nature of the substituent ortho to the phenolic OH plays an important role in determining the course of the reaction. Infrared absorption spectra are given. MeNH2 (0.2 mole) added (cooling) to 12 g. paraformaldehyde in 60 cc. MeOH containing 0.1 g. KOH, the mixture treated with 48.8 g. 2,4-Me2C6H3OH in 60 cc. MeOH, refluxed 2 hrs. and evaporated at room temperature yielded 51 g. N,N-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine [α2,α2'-(methylimino)dimesitol], m. 124-5° (all m.ps. uncor.). For other similarly prepared (3,5,6,2-R1,R2,R3(HO)C6HCH2)2NR, R, R1, R2, R3, yield (%), m.p., and m.p. of the HCL salt are: cyclohexyl, Me, Me, H, 52, 146-7°, 213-15°; HOCH2CH2, Me, Me, H, 60, 128-9°, 185-6°; Me, Cl, Me3C, H, 52, -, 169-71°; cyclohexyl, Cl, CMe3, H, 59, 167-8°, 149-50°; Me, Me3C, Me3C, Me, 55, 130-1°, -. Cyclohexylamine (9.9 g.) added portionwise with cooling to 10 cc. MeOH containing 6 g. paraformaldehyde and 0.05 g. KOH, the solution added to 30 g. p-Me3CC6H4OH in 10 cc. MeOH, the mixture let stand 1 day at room temperature, 50 cc. C6H6, 8 g. NaOH, and 450 cc. water added, the aqueous layer extracted with C6H6, and the combined exts. evaporated in vacuo yielded 24.6 g. 3,4-dihydro-3-cyclohexyl-6-tert-butyl-1,3,2H-benzoxazine, m. 93-4°. Cyclohexylamine (4.95 g.) added to 3 g. paraformaldehyde in 8 cc. MeOH containing 0.05 g. KOH, the solution added to 17.3 g. p-BrC6H4OH in 15 cc. MeOH, the mixture let stand 18 hrs. at room temperature, and the solvent removed in vacuo yielded 35% 3,4-dihydro-3-cyclohexyl-6-bromo-1,3,2H-benzoxazine, m. 91-2°. Paraformaldehyde (2.4 g.) in 5 cc. MeOH containing 0.1 g. KOH (cooled) treated with 4.96 g. 25% MeNH2, then with 7.4 g. 6-chlorothymol (Me = 1) in 8 cc. MeOH, the mixture refluxed 3 hrs., extracted with C6H6, and the C6H6 evaporated yielded 9 g. 3,4-dihydro-6-chloro-3,5-dimethyl-8-isopropyl-1,3,2H-benzoxazine (I), b0.3 120-2°. I (2.2 g.), 5 cc. 20% HCl, and 25 cc. EtOH distd. (30 cc. 50% EtOH and 10 cc. water added during the distillation) until 20 cc. remained and the residue diluted with 20 cc. water yielded 1.1 g. N-methyl-5-chloro-2-hydroxy-6-methyl-3-isopropylbenzylamine-HCl (2-methylaminomethyl-6-chlorothymol-HCl), m. 172-4°, N,N-Bis(4-hydroxy-3,5-dimethoxybenzyl)cyclohexylamine (65% yield), m. 141°. N,N-Bis(4-hydroxy-3,5-dimethoxybenzyl)amine, m. 137°.

ACCESSION NUMBER: 1953:54814 CAPLUS
DOCUMENT NUMBER: 47:54814
ORIGINAL REFERENCE NO.: 47:9292e-i,9293a
TITLE: N,N-Bis(hydroxybenzyl)amines: synthesis from phenols, formaldehyde, and primary amines
AUTHOR(S): Burke, W. J.; Smith, Richard P.; Weatherbee, Carl
CORPORATE SOURCE: Univ. of Utah, Salt Lake City
SOURCE: Journal of the American Chemical Society (1952), 74, 602-5
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 47:54814

L7 ANSWER 38 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB The condensation of 2-C10H7OH (I) with formaldehyde and aliphatic and alicyclic primary amines yielded 2,3-dihydro-2-substituted-1H-naphth-[1,2-e]-m-oxazines (II) or N, N-bis(2-hydroxy-1-naphthylmethyl)alkylamines (III) depending upon the reaction conditions. The II were readily split by acids to yield the corresponding 1-(substituted aminomethyl)-2-naphthols. To 12.4 g. 25% aqueous MeNH2 in 60 cc. MeOH were added with cooling 18.5 cc. 37% aqueous CH2O in 40 cc. MeOH and 14.4 g. I in 50 cc. MeOH, and the mixture was gently refluxed 1.5 h. and poured into 400 cc. cold H2O to yield 19.6 g. (98%) 2,3-dihydro-2-methyl-1H-naphth[1,2-e]-m-oxazine (V), m. 67-8° (from MeOH); HCl salt, m. 185-7° (decomposition), obtained in quant. yield from V in cold Me2CO with 1 equivalent concentrated HCl.
The following II (2-alkyl group given) were prepared similarly: PhCH2 (VI), 99.5%, white prisms, m. 126-7° (from EtOAc) [HCl salt, m. 169-70° (decomposition)]; Bu, 87%, oil [HCl salt, m. 138-40°]; cyclohexyl (VII), quant., oil [HCl salt, m. 178-9° (decomposition)]. VII (4 g.) and 1.0 cc. concentrated HCl in 60 cc. 85% PrOH were distd., while 25 cc. PrOH was being added, until the CH2O was removed, 60 cc. Me2CO was added, and the mixture cooled to give 3.65 g. (93%) 1-cyclohexylaminomethyl-2-naphthol-HCl, m. 192-3° (decomposition) (from EtOH). The following III-HCl (alkyl given) were prepared similarly: PhCH2, 86%, m. 170-2° (from MeOH); Bu, 60%, m. 143-5° (from 50% aqueous MeOH); Me (VIII), 94%, m. 202-4° (decomposition) (from EtOH). To 28.8 g. I and 15 cc. 37% aqueous CH2O in 75 cc. MeOH was added dropwise 12.4 g. 25% aqueous MeNH2 in 50 cc. MeOH and the mixture let stand 24 h. at room temperature to give 31.2 g. (91%) 1,1'-bis(2-hydroxy-1-naphthyl)trimethylamine (IX), m. 147-8° (from HCONMe2-MeOH); HCl salt + 1 mol. MeOH, m. 142-4° (from MeOH), from IX in MeOH and excess concentrated HCl; HCl salt, m. 148-51° (decomposition). Similarly were prepared the following III (alkyl given): Bu, 64%, white prisms, m. 137-8° (from HCONMe2-MeOH) [HCl salt, m. 135-7° (from aqueous MeOH)]; cyclohexyl (X), 86%, m. 120-2° [HCl salt, m. 172-4° (from MeOH)]. The condensation of equimol. quantities of MeNH2, CH2O, and I at 25° gave 82% IX; similarly was obtained from cyclohexylamine (XI) 59% X. A 1:2:1-mol. ratio of MeNH2-CH2O-I condensed at 0° gave 79% IX and 20% V, at 25° 58% V and 39% IX. A similar condensation of a 1:2:2 mol. XI-CH2O-VI mixture at 60° yielded 55% VII. To 1.0 g. VI in dry Et2O was added a large excess of PhMgBr and the resulting precipitate in 15 cc. EtOH treated with 3 cc. concentrated HCl to yield 0.1 g. (8%) 2-HOC10H6CH2N(CH2Ph)2, m. 115-17°, also obtained in 62% yield by refluxing 1.5 h. 3 g. VIII and 8.0 g. (PhCH2)2NH in 40 cc. EtOH. IX (3 g.), 12.4 g. 25% aqueous MeNH2, and 15 cc. 37% CH2O in 100 cc. MeOH gently refluxed 1.5 h. gave 3.4 g. (98%) V. In a similar run with PhCH2NH2, VI was obtained in 97% yield. To 5.8 g. IX in 70 cc. AcOH was added at 0° 2.3 cc. aqueous HNO3 and after 5 min. 200 cc. H2O to give 1,2-O2NC10H6OH, m. 102-3°. A similar nitration of IX at 25° gave 63% 1,6,2-(O2N)2C10H5OH, m. 193-4°. IX (3.43 g.) treated 2 wk at room temperature with 10 g. Ac2O and 20 cc. pyridine, and the mixture poured into 200 cc. H2O gave 4.3 g. diacetate (XII) of IX, m. 158-60° (from EtOH). Hydrolysis of XII with 2% KOH in MeOH at 25° gave IX. IX (5 g.) in 30 cc. Ac2O heated 8 h. at 125°, and the mixture made alkaline with 2 g. excess KOH in 150 cc. MeOH, refluxed 2 h., cooled, and acidified with concentrated HCl precipitated 2.9 g. (86%) N-methyl-N-(2-hydroxy-1-naphthylmethyl)acetamide (XIII), m. 199-200° (from

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EtOH), sol. in dil. aq. alkali, gives a greenish yellow color with alc. FeCl3. XIII (2.9 g.) in 12 cc. Ac2O heated 8 h. at 100-10° gave 3.1 g. (90%) O-Ac deriv., m. 123-5° (from aq. MeOH). The N-CH2Ph analog of XIII, m. 169-70° (from EtOH), was prepd. similarly in 37% yield from VI and Ac2O at 130°. IX (3 g.) in 30 cc. H2O contg. 4 g. KOH refluxed 30 min. and the mixt. dild. with 200 cc. H2O and acidified with HCl gave 2.4 g. (2-HOC10H6)2CH2, m. 202-3°. Condensation of 9.9 g. XI with 15 cc. 37% CH2O in 100 cc. MeOH and 14.4 g. 1-C10H7OH in 100 cc. MeOH at -5 to 0° yielded 18.0 g. (67%) 3,4-dihydro-3-cyclohexyl-2H-naphthol[2,1-e]-m-oxazine (XIV), m. 86-8° (from Me2CO), decompd. by heating in MeOH or Me2CO. XIV (11.2 g.) and 5.0 cc. concd. HCl in 50 cc. EtOH refluxed 5 min. gave 79% 2-cyclohexylaminomethyl-1-naphthol-HCl (XV), m. 171-4° (decompn.). XV (1.2 g.) and 1.74 g. piperidine heated 30 min. at 100-10° and dild. with 10 cc. MeOH gave 71% 2-piperidinomethyl-1-naphthol, m. 133-4°.
ACCESSION NUMBER: 1953:31863 CAPLUS
DOCUMENT NUMBER: 47:31863
ORIGINAL REFERENCE NO.: 47:5408h-i,5409a-h
TITLE: Condensation of naphthols with formaldehyde and primary amines
AUTHOR(S): Burke, W. J.; Kolbezen, Martin J.; Stephens, C. Wayne
CORPORATE SOURCE: Univ. of Utah, Salt Lake City
SOURCE: Journal of the American Chemical Society (1952), 74, 3601-5
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 47:31863

L7 ANSWER 39 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB The methylation of PhNH2, o- (I) and p-MeC6H4NH2 (II), 5,2-BrMeC6H3NH2 (III), o-ClC6H4NH2 (IV), and 2,6- (V) and 2,4-xylidine (VI) with (HCHO)n and HCO2H, HCl, HBr, or AcOH, or without acid shows that, without acid, only negligible condensation takes place. Heating PhNMe2, (HCHO)n, and 98% HCO2H (1:1:1) 1 hr. gives 92% (p-Me2NC6H4)2CH2, m. 85-6°; p-MeC6H4NMe2, (HCHO)n, and HCO2H (1:1:1), heated 3.5 hrs., give 98% [5,2-Me(Me2N)C6H3]2CH2. Heating V, (HCHO)n, and HCO2H (1:3:3) 0.5 hr. gives 33% 2,6-Me2C6H3NMe2, b. 194-9°, and 63% diphenylmethane base, b0.8 170.5°, m. 49.5-50.5°, resolidifying and m. again 60-60.5°; 2,6-Br2C6H3NH2 (VII), (HCHO)3, and HCO2H (1:3:8), heated 3 hrs., give 83% [3,5,4-Br2(H2N)C6H2]2CH2, m. 159-60°; m-O2NC6H4NH2 (VIII), (HCHO)n, and HCO2H (1:2.6:4), heated 10.5hrs., give [4,2-Me2N(O2N)C6H3]2CH2, m. 191-2°. II, (HCHO)n, and HCO2H (1:3:3), heated 0.5 hr., give a trace of p-MeC6H4NMe2 and 10% 3-p-tolyl-6-methyl-3,4-dihydroquinazoline, m. 156.5-7°. VI (0.2 mol.) added to (HCHO)n and HCO2H (1:3:3) reacts vigorously; when the mixture is heated 0.5 hr. 33% 2,4-Me2C6H3NMe2 and an unidentified compound, b0.8 186-7°, m. 165-6°, are formed. Similarly, 2,4-Cl2C6H3NH2 (IX), (HCHO)n, and HCO2H (1:3:3) give 84% 2,4-Cl2C6H3NMe2, m. 169.5-70.5°, which is changed when refluxed with Ac2O alone or with C5H5N. The rate of methylation is measured by determining the CO2 formed. After an extensive study of the effect of the amount of HCHO, of H2O, of variation in the amts. of HCO2H, of strong acids, of the order of mixing the reagents, and of agitation, the results of which are given in 5 tables, a modified procedure for the Wallach methylation of aromatic amines is given: 1 mol. amine is added gradually to a gently warmed and stirred mixture of 2.5 mols. (HCHO)n and 3 mols. HCO2H, the mixture heated 5 min. on a steam bath, poured into ice-cold NaOH (1.3 equivs. to 1 of the HCO2H) and Na2SO3 (1.2 equivs. to 1 of the HCHO), the solution steam-distilled, and the distillate extracted with ether. In this way the following amines give the corresponding N,N-di-Me derivs. (% yield): I 40, II 50, IV 23, p-isomer 65, VI 65, V 97, p-O2NC6H4NH2 50, p-MeOC6H4NH2 50, mesidine 98, IX 92, VII 92, 2,4-MeBrC6H3NH2 98, 2,4,6-Br3C6H2NH2 98, o-MeC6H4NHMe 55, p-isomer 95, 2,4-Me2C6H3NHMe 98, 2,6-isomer 98. PhNH2, m-MeC6H4NH2, 1- and 2-C10H7NH2, p-H2N'C6H4SO3H, VIII, PhNHMe, and m-MeC6H4NHMe are not methylated by this procedure. The primary and secondary amines successfully methylated all have 1 or more of the o- and p-H atoms replaced. With all reactive positions unsubstituted, the nuclear condensations predominate; with 1 or 2 reactive positions blocked, methylation reaches 90%; with all reactive positions blocked, methylation is almost 100%.
ACCESSION NUMBER: 1953:28627 CAPLUS
DOCUMENT NUMBER: 47:28627
ORIGINAL REFERENCE NO.: 47:4854a-g
TITLE: Methylation of aromatic amines by the Wallach method
AUTHOR(S): Borkowski, Walter L.; Wagner, E. C.
CORPORATE SOURCE: Univ. of Pennsylvania, Philadelphia
SOURCE: Journal of Organic Chemistry (1952), 17, 1128-40
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 47:28627

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AB cf. C.A. 43, 3425e. Dropwise addition of 0.1 mole PhCH2NH2 to 0.22 mole aqueous 37% CH2O in 50 cc. dioxane at 15-18°, then 0.03 mole phloroglucinol dihydrate, refluxing 1.5 hrs., evaporation of solvent, and crystallization of the residue from 9:1 C6H6-EtOH gave 48% 3,4,6,7,8,10,11,12-octahydro-3,7,11-tribenzyl-2H-benzo[1,2-e,3,4-e',5,6-e'']tris-m-oxazine, m. 162-3°, insol. in MeOH and 40% aqueous MeOH, partially soluble in hot EtOH, soluble in aqueous HCl, C6H6, and hot CCl4 and EtOAc. A series of bis-m-benzoxazines was prepared similarly (read amine used, phenol, m.p., and % yield): MeNH2, pyrocatechol, 174-5°, 45; PhCH2NH2, pyrocatechol, 182-3°, 48 (Ia); cyclohexylamine, pyrocatechol, 143-4°, 29; MeNH2, hydroquinone, 182-3°, 61; cyclohexylamine, hydroquinone, 161-2°, 31 (Ib); PhCH2NH2, toluhydroquinone, 105°, 58. Solution of 0.4 g. 2,3,4,7,8,9-hexahydro-3,8-dimethylbenzo[1,2-e,4,5-e']bis-m-oxazine (I) in 20 cc. warm 95% EtOH, cooling, addition of 4 cc. concentrated HCl at 0°, and slow distillation of the EtOH with addition of 20 cc. H2O gave 72% 2,5-bis(methylaminomethyl)hydroquinone-2HCl, m. 269-70° (from H2O). The distillate contained CH2O. Dropwise addition of 0.2 mole 85% HCO2H to 0.011 mole I at 0°, then 3.8 cc. 37% CH2O, heating to 90°, cooling to 70° during 30 min. (gas evolution), heating 2 hrs. at 90°, 12 hrs. at 85°, cooling, addition of 5 cc. concentrated HCl, concentration in vacuo to a solid, solution in aqueous Na2CO3, and extraction with EtOAc gave 71% 2,5-bis(dimethylaminomethyl)hydroquinone (IIa), m. 190-1°. Addition of 0.22 mole cyclohexylamine during 2 min. to 0.22 mole 37% CH2O in 75 cc. dioxane, then 0.1 mole hydroquinone, refluxing 2.5 hrs., and concentration gave 35% 2,5-bis(cyclohexylaminomethyl)hydroquinone (II), m. 173-4°. Addition of 0.0053 mole 37% CH2O to 0.0015 mole II in 50 cc. cooled dioxane, 2 hrs. at 55°, 1 hr. at room temperature, and concentration gave 86% Ib. Ia (6 g.) and 15 cc. Ac2O heated 2 hrs. at 90-5°, 2 hrs. at 80°, and allowed to stand 3 hrs. at room temperature gave a brown viscous precipitate; addition of excess NaHCO3 and CHCl3 extraction gave 3 g. 2,5-bis[(N-acetylcyclohexylamino)methyl]hydroquinone, m. 290° (decomposition). 2,5-Bis[(N-acetylmethylamino)methyl]hydroquinone, similarly prepared from I, m. 273-5°. MeMgBr gave no gas evolution with dry C6H6 solns. of I, Ia, or Ib, but did give a definite gas evolution with II and IIa. I and Ib gave no H with Na in C6H6.
ACCESSION NUMBER: 1951:13892 CAPLUS
DOCUMENT NUMBER: 45:13892
ORIGINAL REFERENCE NO.: 45:2487i,2488a-e
TITLE: 3,4-Dihydro-1,3,2H-benzoxazines. Reaction of polyhydroxybenzenes with N-methylolamines
AUTHOR(S): Burke, W. J.; Weatherbee, Carl
CORPORATE SOURCE: Univ. of Utah, Salt Lake City
SOURCE: Journal of the American Chemical Society (1950), 72, 4691-4
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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GI For diagram(s), see printed CA Issue.

AB A large number of thiazolidine (I) derivs. were prepared as model compds. to study their stability in solution, cleavage by mercuric and other salts, electrometric and polarog. behavior, etc. The compds. were prepared by: (1) condensation of **penicillamine** (II) or its esters with aldehydes, their acetals, or Schiff bases or ketones; (2) condensation of the Et ester of II with MeCSNH2 and reduction of the 4-carbethoxy-2,5,5-trimethylthiazoline (III) obtained with Al-Hg in moist ether; (3) addition of Me2C:CO to derivs. of 2-thiazoline, followed by hydrolysis to yield 2,3-disubstituted derivs. of I; (4) the reaction of β-mercapto-α-amino acids with 4-alkoxy- or 4-(hydroxymethylene)oxazolones under conditions such that concomitant opening of the oxazolone ring occurred to give I. Azothiazolidines: An attempt was made to synthesize α-amino-4-carboxy-5,5-dimethyl-2-thiazolidineacetic acid (IV) as a possible route to the penicillic acids or the penicillins. The 1st method consisted in coupling diazotized p-ClC6H4NH2 with OHCCHNaCO2Et to p-ClC6H4N2CH(CHO)CO2Et (V) and coupling V with DL-II.HCl to the azo ester (VI), S.CMe2.CH(CO2H).NH.CHCH(CO2Et)N:NC6H4Cl. Chemical methods of reduction (Zn dust in AcOH and alkaline Na hyposulfite) were resorted to, for no success was achieved by hydrogenation with various catalysts. Expts. in which the product from these chemical redns. was freed from p-ClC6H4NH2, phenylthioacetylated, and then submitted to azlactonization (shaking with Ag2O in ether), yielded materials devoid of penicillin activity. As an alternative route to compds. of type IV, EtOCH:C(NO2)CO2Me (VII) was prepared II plus VII did not give a derivative of I. Attempted conversion of imidazolidines to thiazolidines. In order to determine whether the proposed conversion of imidazolidines to I could be realized, II.HCl and 2-[carbethoxy(p-chlorophenylazo)methyl]-1,3-dibenzylimidazolidine (VIII) were refluxed in aqueous MeOH, giving 2-[carbethoxy(p-chlorophenylazo)methyl]-5,5-di-methyl-4-thiazolidinecarboxylic acid. A similar exchange reaction with **ethanolamine** gave the corresponding oxazolidine. The latter could be converted to derivs. of I by treatment with II.HCl. Some properties of thiazolidines: I derivs. undergo N-substitutions with the usual acylating reagents, such as ClCO2CH2Ph, ketenes, etc. N-Alkylation can be effected with MeI and Na in liquid NH3. Many I compds. are cleaved by excess Na in liquid NH3 to N-alkylated cysteines or penicillamines. Desulfurization of I by Raney Ni proceeded easily in aqueous NaHCO3. Stability of thiazolidines: A number of derivs. of I, RR'C.S.CMe2.CH(CO2H).NR''(IX), were examined for comparison with penicillin and its derivs. Where R and R' = Me and R''= H, a deep blue FeCl3 color immediately formed upon boiling an aqueous solution, indicating hydrolysis to a thiol compound Where R and R''= H and R' = Et, hydrolysis occurred only after boiling 1-2 min., while when R, R', and R''= H, no hydrolysis occurred even after 3 h. The stabilities of several thiazolidines were compared with reference to HCHO and BzH. The principal result was that, as a class, 2-alkyl-4-carboxylic acid derivs. of I were stable to both of the aldehydes, while 2,2-dialkyl-4-carboxylic acids were readily decomposed Oxidation studies on thiazolidines: Thiazolidines containing a free NH group were oxidized by Na metaperiodate with rupture of the ring, followed by oxidation of the liberated **mercaptoamine** at the thiol group. The 3-acetylthiazolidines, in which the thiazolidine ring is more stable, were

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simply oxidized to the corresponding sulfoxides. Reaction of some thiazolidines with CS2 or COCl2: S.CMe2.CH(CO2Me).NH.CHCH2NH2 (X) with CS2 gave S.CMe2.CH(CO2Me).N.CH.CH2.NH.CS (XI) and S.CMe2.CH(CO2Me).N.CH.CH2.S.C:NH (XII). With COCl2 in the presence of NaHCO3, X gave only S.CMe2.CH(CO2Me).N.CH.CH2.NH.CO (XIII). 3-(2-Hydroxyethyl)thiazolidines: Thiazolidines contg. a free NH group with ethylene oxide in the presence of BF3 gave 3-(2-hydroxyethyl) derivs. In the case of **isopropylidenepenicillamine** the product isolated was the lactone, Me2C.S.CMe2.CH.N.CH2.CH2.O.CO (XIV). No reaction was obsd. between Me benzylpenicillin and ethylene oxide. Misc. phenylpenilloic and penicilloic derivs. and some N-alkyl and N-aralkyl compds.: Formylation of Et hippurate afforded Et formylhippurate and Et hippurylhippurate. The di-Et acetal of the former was more satisfactory for condensation with II, giving α-Et phenylpenicilloate, which hydrolyzed to phenylpenicilloic acid. The latter was, however, readily decarboxylated to phenylpenilloic acid and with Ac2O gave no evidence of dehydration, but rather of acetylation, and no significant biol. activity was produced. A no. of other syntheses were initiated in the hope of synthesizing a **N-Me** or N-benzyl analog of "tricyclic penicillin," S.CMe2.CH(CO2H).N.CH.CH.NH.CR.O.CO (XV) since some of the reactions could equally well have given the corresponding analogs of the β-lactam formula. Exptl.: An example of each general procedure for prepn. of derivs. of I will be given. (1) Cysteine Et ester-HCl was refluxed in abs. EtOH contg. a trace of HCl with a slight excess of paraformaldehyde; 4-carbethoxythiazolidine-HCl, m. 144-5°, crystd. on addn. of ether to a warm EtOH soln. (2) DL-II Et ester-HCl (1.5 g.) and 0.6 g. MeCSNH2 were finely ground and heated 30 min. at 100°, then 2-5 h. at 120° (H2S was evolved and NH4Cl sepd.), the melt extd. with ether (3 + 15 cc.), and the dried ext. concd. and treated with dry HCl-Et2O, giving 4-carbethoxy-2,5,5-trimethyl-2-thiazoline-HCl, small rods from CHCl3-ether, subliming at 80-90° (14 mm.) in long white deliquescent needles, m. 140-1°. The free base (350 mg.), b0.1 60-3°, in 80 cc. ether was treated with 2.5 g. amalgamated Al, 8 cc. water added in portions over 3 days, the ether evapd., the oil dried over P2O5, dissolved in dry ether, and treated with dry HCl, giving 250 mg. 4-carbethoxy-2,5,5-trimethylthiazolidine-HCl, m. 113-14° (from CHCl3-ether). (3) Me2C:CO (10.5 g.) and 7.6 g. 2-methyl-2-thiazoline in 100 cc. cold EtOAc were stoppered under N, left for 3 days, the soln. extd. with aq. NaHCO3, washed, dried, and evapd., the residue dissolved in 50 cc. light petroleum, filtered, concd. to a light yellow oil (23 g.), the latter refluxed for 18 h. in 50 cc. EtOAc, 15 cc. water, and 2 cc. AcOH, acidic materials extd. with aq. NaHCO3, and the ext. washed and acidified, giving an oil which crystd. on cooling and scratching; recrystn. from aq. MeOH gave 2-methyl-2-(1-carboxyisopropyl)-3-isobutyrylthiazolidine, m. 130.5°. (4) Cysteine Me ester-HCl (1.71 g.) and 2.1 g. 2-benzyl-4-methoxymethylene-5(4H)-oxazolone heated in 50 cc. pyridine on the steam bath for 10 min., the pyridine evapd., the residue dissolved in CHCl3, and the ext. washed with water, and evapd. gave 2-[(α-1,1-phenylacetamido) carbomethoxymethyl]-4-carbomethoxy-1-thiazolidine, m. 188-9° (from EtOAc). Phys. properties of the remainder of the compds. prepd.: D-2-phenyl-4-carboxy-5,5-dimethylthiazolidine, m. 151.5-52° (decompn.); α-Me D-γ-benzylpenicilloate, [α]D25 31° (c 25%, MeOH), obtained as a glass; 2-keto-5-carboxy-6,6-dimethyl-4-thiazane, m. 182-4° (decompn.); 3-keto isomer, m. 171-4°; 2-[(α-phenylacetamido)methyl]-4-carbomethoxy-5,5-dimethyl-2-thiazoline, b0.1 180-90°; 2-(1-carboxyisopropyl)-3-isobutyrylthiazolidine, m. 122°; 2-phenyl-2-(1-carboxyisopropyl)-3-isobutyrylthiazolidine (XVI), m. 157.5-58°; 6,1,2',3'-thiazolidino-

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6-phenyl-3,3,5,5-tetramethyl-2,4-piperidinedione, m. 136-7°; XVI Me ester, m. 137-8°; D-2-(1-carboxyisopropyl)-3-isobutyryl 4-carbomethoxy-5,5-dimethylthiazolidine, m. 147-9°; 6,-1,2',3'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-6-phenyl-3,3,5,5-tetramethyl-2,4-piperidinedione, m. 154°; L-isomer, m. 99-102°; 3-acetyl-4-carbomethoxy-5,5-dimethylthiazolidine, yellow oil; Me phenylpenilloate, b0.05 120°; phenylpenilloic acid-HCl, m. 220°; DL-2-[benzamido(benzylcarbamyl)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine, m. 205°, with softening from 190°; DL-2-[(α-phenylacetamido) (1-carbomethoxy-2-mercapto-2,2-dimethylethylcarbamyl)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine, m. 212-13°; D-2-[(α-phenylacetamido) (phenethylcarbamyl)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine, m. 175-6°; D-2-[(α-phenylacetamido)benzylcarbamylmethyl]-4-benzylcarbamyl-5,5-dimethylthiazolidine, m. 186-8°; DL-2-[(α-phenylacetamido) carbomethoxymethyl]-4-carboxythiazolidine, m. 155.5-56°; L-form, m. 160-1°; DL-2-[(α-phenylacetamido)carbethoxymethyl]-4-carboxythiazolidine, m. 188°; L-2-[(α-phenylacetamido)carbobenzyloxymethyl]-4-carboxythiazolidine, m. 160-2°; D-heptylpenilloic acid-HCl, m. 190-1°; D-2-[(α-cyclohexylacetamido)carbethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 182-3°; D-2-[benzamido(carbomethoxy)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine-HCl, m. 190°; DL-2-[(α-phenylacetamido)carbomethoxymethyl]-3-formyl-4-carboxy-5,5-dimethylthiazolidine, m. 175°; D-2-[(α-phenylacetamido)carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 159-60°; α-Et D-benzylpenicilloate, m. 150° (decompn.); **benzylamine** salt of α-benzyl D-benzylpenicilloate, m. 163-4°; L-2-[(α-(p-acetoxyphenyl)acetamido]carbethoxymethyl)-4-carbethoxythiazolidine, m. 55-60°; L-2-[(α-(p-methoxyphenyl)acetamido]carbomethoxymethy l)-4-carboxythiazolidine, m. 165-6°; D-2-[(α-(p-methoxyphenyl)acetamido]carbomethoxymethyl)-4-carboxy-5,5-dimethylthiazolidine, white powder; 2-[(p-chlorophenylazo)carbethoxymethyl-4-carboxy-5,5-dimethylthiazolidine], m. 152°; Me (ethoxymethylene)nitroacetate, b12 156-7°; Me (anilinomethylene)nitroacetate, m. 109-9.5°; p-(chlorophenylazo)-formylacetic acid, m. 104-5°; 2-[(p-chlorophenylazo)-carboxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 165-6° (pyridine salt, m. 149°); Et β,β-diethoxy-α-(p-chlorophenylazo)propionate, m. 54-5°; DL-2-α-(2-hydroxynaphthyl)-4-carboxy-5,5-dimethylthiazolidine, m. 129-30°; DL-2-(3-methoxy-4-hydroxyphenyl)-4-carboxy-5,5-dimethylthiazolidine, m. 184° (decompn.); DL-2-(2-hydroxyphenyl)-4-carboxy-5,5-dimethylthiazolidine, m. 180-1°; DL-2-[(p-chlorophenylazo)carboxymethyl]-4-carboxy-3,5,5-trimethylthiazolidine, m. 182°; 2-[(p-chlorophenylazo)carbethoxymethyl]-1,3-dibenzylimidazolidine, m. 88-9°; 2-[(p-chlorophenylazo)carbethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 150°; 2-[(p-chlorophenylazo)carbethoxymethyl]-1,3-dibenzyl-4-imidazolidinecarboxylic acid, m. 137°; 2-styryl-1,3-dibenzylimidazolidine, m. 117°; 2-propenyl analog, m. 85.5-6°; 2-phenyl-4-(4-morpholinylmethylene)-5(4H)-oxazolone, m. 167°; 2-phenyl-5,5-dimethyl-4-thiazolidinecarboxylic acid, m. 141-2°; 2-[(p-chlorophenylazo)carbethoxymethyl]-5,5-dimethyl-4-thiazolidinecarboxylic acid, m. 151-2°; 2-(formamidocarbethoxymethyl)oxazolidine, m. 123.5-4.5°; 2-[(p-chlorophenylazo)carbethoxymethyl]-oxazolidine, m. 145-6°; L-4-carboxy-2,2,3,5,5-pentamethylthiazolidine-HCl, m. 220-1°

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(decompn.); N-acetyl-N-benzylalanine, m. 103-5°; Me [2-(α-phenylacetamido)-2-carboxyethylcarbamyl]-β,β-dimethylpropionate, m. 142°; L-**N-methylpenicillamine**, m. 208-10° (HCl salt, m. 80-120°); L-4-carboxy-3,5,5-trimethylthiazolidine-HCl, m. 191-2°; L-3-methyl-4-carboxythiazolidine-HCl, m. 180-1°; L-**N-methylpenicillamine**-HCl, m. 160-70° (decompn.); L-N-isopropylcysteine-HCl, hygroscopic; α-Me N4-methyl-L-benzylpenicilloate, m. 165-7.5° (decompn.) [for numbering, see formula (XVIa) below]; L-2-[(α-phenylacetamido)-carbobenzyloxymethyl]-3-methyl-4-carboxythiazolidine, m. 180° (decompn.); **benzylamine** salt of α-Et N4-methyl-L-benzylpenicilloate, m. 80-3°; 2-phenyl-4-carboxythiazolidine, m. 158°; 2-phenyl-4-carboxy-5,5-dimethylthiazolidine, m. 152-3°; 2-phenyl-3-acetyl-4-carboxy-5,5-dimethylthiazolidine sulfoxide, m. 136° (decompn.); sulfone, m. 207-8° (decompn.); 2-phenyl-3-acetyl-4-carboxythiazolidine sulfoxide, m. 130-2°; sulfone, m. 198-200°; DL-3-chloroacetyl-4-carbomethoxy-5,5-dimethylthiazolidine sulfone, m. 110-11°; D-2-isopropyl-3-benzoyl-4-carbomethoxy-5,5-dimethylthiazolidine sulfone, m. 119-20°; D-2-phenyl-3-benzoyl-4-carbomethoxy-5,5-dimethylthiazolidine sulfone, m. 200°; 2,2-diethoxyethyl isothiocyanate, b2 63-5° (phenylthiourea deriv., m. 96°; benzylthiourea deriv., m. 60°; treatment of the isothiocyanate with 2,4-(O2N)2C6H3NHNH2 gave 2,4-(O2N)2C6H3NHN:CHCH2NHCSNHNHC6H3(NO2)2, m. 250-2°; 3-(2,2-diethoxyethyl)-5-isopropylidene-2-thiohydantoin, m. 87-8° (2,4-dinitrophenylhydrazone, m. 230-2°); Et α-(3-phenylthioureido)-β-mercapto-β,β-dimethylpropionate, m. 81°; 3-phenyl-5-(1-mercaptoisopropyl)-2-thiohydantoin, m. 165° (decompn.); 5-isopropylidene analog, m. 254-7°; 2-carbomethoxymethyl-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 149-50° (decompn.); 1,5,3',4'-(2'-carbethoxymethyl-5',5'-dimethylthiazolido)-3-phenyl-2-thiohydantoin, m. 123°; 6,1,2',3'-(4'-carboxy-5',5'-dimethylthiazolido)-3-phenyl-5,6-dihydro-2-thiouracil, m. 215-17°; 2-aminomethyl-4-carbomethoxy-5,5-dimethylthiazolidine, b0.005 104-6°; 4,3,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolido)-2-imidazolidone, m. 124-5°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolido)-2-iminothiazolidine, m. 187-8°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolido)-2-imidazolidinethione, m. 117-18°; 3,4,3',2'-(4'-carboxy-5',5'-dimethylthiazolido)-2-iminothiazolidine, m. 197-8°; 3,4,3,',2'-(4'-carbomethoxy-5',5'-dimethylthiazolido)-2-imino-5-carbomethoxythiazolidine, m. 219°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolido)-5-carbomethoxy-2-imidazolidinethione, m. 162°; 2-methylaminomethyl-4-carboxy-5,5-dimethylthiazolidine-2HCl, m. 207-8°; the lactone of 3-(2-hydroxyethyl)-4-carboxy-2,2,5,5-tetramethylthiazolidine, m. 102°; N-(2-hydroxyethyl)-**penicillamine**-HCl, m. 148° [free base, m. 174° (decompn.)]; 3-(2-hydroxyethyl)-4-carbomethoxy-2,2,5,5-tetramethylthiazolidine, m. 48-9° (lactone, m. 100°); 2-phenyl-3-(2-hydroxyethyl)-4-carboxy-5,5-dimethylthiazolidine, m. 129° (lactone, m. 104-5°); 2-[(caproylamino)carbethoxymethyl]-3-(2-hydroxyethyl)-4-carboxy-5,5-dimethylthiazolidine, m. 127-8° (lactone, m. 132-3°); α-Et β-Me amylpenicilloate-HCl, m. 125-7°; α-Et N4-(2-hydroxyethyl)benzylpenicilloate, m. 139-40° (lactone, m. 153-4°); lactone of 2-(α-phenylacetamido)-methyl-3-(2-hydroxyethyl)-4-carboxy-5,5-dimethylthiazolidine, m. 166°; the butanolate of N4-(2-hydroxyethyl)benzylpenicilloic acid, m. 117-18°; lactone of

N-(2-hydroxyethyl)benzylpenicilloic acid, m. 175°; bis(benzylammonium) salt of N4-(2-hydroxyethyl)benzylpenicilloic acid, m. 131-2°; benzylammonium salt of the corresponding lactone, m. 255-7°; N-benzyl-α-phenylacetamide, m. 116-17°; the hydrazinium salt of N4-(2-hydroxyethyl)benzylpenicilloic acid α-hydrazide, m. 163-4°; N4-(2-hydroxyethyl)benzylpenicilloic acid dihydrazide, m. 205° (decompn.); lactone of the α-benzylamide of N4-(2-hydroxyethyl)benzylpenicilloic acid, m. 200-2°; Et hippurylhippurate, m. 128-9°; Et formylhippurate 2,4-dinitrophenylhydrazone, m. 175-6°; Et formylhippurate di-Et acetal, b0.1 150-3°; α-Et phenylpenicilloate-HCl, decompd. at 105°; phenylpenicilloic acid, m. 96-7°; N-acetylphenylpenilloic acid, m. 190-1° (decompn.). N-Alkyl and N-aralkylthiazolidines: 2-[(Methylamino)-carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine-HCl, hygroscopic, amorphous solid; Me N-methylphenylpenaldate, m. 144-6°; treatment with aniline gave the anil, m. 204-5°; Et N-methylhippurate , b0.1 118°, m. 33.5°; N-methylhippuric acid, m. 104-5°; Et N-methylphenylpenaldate, m. 129-30°; anil, m. 179°; benzylimine, m. 154°; N-benzyl-N-formylglycine Et ester, b0.05 128-32°; Et α-(N-formylbenzylamino)-β-hydroxyacrylate, m. 89°; enol benzoate, m. 60°; enol acetate, m. 74°; N-benzyl-β,β-diethoxyalanine, m. 167-8°; N-benzylbenzylpenaldic acid di-Et acetal, m. 103-4°; Et N-benzylhippurate, m. 58-60°; N-benzylhippuric acid, m. 109-10°; Et N-benzylphenylpenaldate, m. 136.5-7.5°; anil, m. 117-18°; benzylimine deriv., m. 117-18°; Et α-(N-benzylbenzamido)-β-(carboxymethylamino)-acrylate, m. 180-1°; Et N-benzyl-N-caproylglycine, b0.08 132-4°; Et α-(N-benzylcaproylamino)-β-benzylaminoacrylate, b0.001 125-35°; benzylimino deriv., m. 75°; Et N-methylaceturate, b0.01 80-4°; Et N-methylmethylpenaldate, m. 45-7°; anil, m. 141°; benzylimine, m. 107-8°; N-benzyl-N-2-hexenoylglycine Et ester, b0.5 150°; N-benzyl-N-3-hexenoylglycine Et ester, b0.2 142-4°; N-benzyl-3-(1-butenyl)-2,4-pyrrolidinedione, m. 114-15°; Et N7-benzyl-DL-amylpenicilloate, viscid gum; treatment with dry HCl in dry ether gave DL-2-[(N-benzylcaproylamino)carbethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 63-71°; Et N7-benzyl-DL-phenylpenicilloate, glassy solid, m. 50-5° (HCl salt, m. 75-84°); benzylamine salt of D-2-[(N-benzyl-α-phenylacetamido)-carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 154-6°; D-2-[(N-methylbenzamido)carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 157-7.5°, [α]D28 28.2° (c 0.8, MeOH); di-Me ester, prepd. with CH2N2, b0.001 110-40°, [α]D28 22.8° (c 0.8, CHCl3); another form of the di-Me ester, m. 115-17°, was prepd. from D-penicillamine Me ester and Me N-methylphenylpenaldate in C6H6; D-2-[(N-methylbenzamido)carboxymethyl]4-carbomethoxy-5,5-dimethylthiazolidine, [α]D28 30.2° (c 0.7, MeOH); D-2-[(N-methylbenzamido)carbeth oxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 152-3°, [α]546125 29.8° (c 1.274, alc.); N-benzylhippuric hydrazide, m. 85-6°; 4-(N-methylbenzamido)-5-pyrazolone, m. 237-40°, with slight softening at 225°; α-{[isopropylidene(carbomethoxy)methylamino]methylen e}-α-(N-methylbenzamido)glycine Et ester, Me2C:C(CO2Me)NHCH:C(NMeBz)CO2Et, m. 146°; α-Et N4-acetyl-N7-methyl-D-phenylpenicilloate (XVIa), m. 156-7°, [α]546125 127.5° (c 1.2, alc.); N4-isobutyryl homolog, m.

197°, [α]546123 60.4° (c 0.612, EtOH); α-Et β-Me N4-isobutyryl-N7-methyl-D-phenylpenicilloate, m. 97°, [α]5461 28° (c 0.5, EtOH); α-Et N4-benzoyl-N7-methyl-D-phenylpenicilloate, m. 224°. Alkyl and aryl thiazolidines: 2-Spirocyclohexyl, m. 165-9°; 2-Ph, m. 105-9°; 2-(p-methoxyphenyl), m. 94-6°. Monocarboxythiazolidine derivs: L-2-Methyl-4-carboxy, m. 162-3° (Et ester-HCl, m. 123-4°); 4-carboxy-5-Me, m. 208-9° (decompn.) [from "B" thiothreonine (Carter, et al., C.A. 35, 5463.3, a 2nd isomer, from "A" thiothreonine, m. 193-4°, was obtained)]; 2,2-dimethyl-4-carbomethoxy, b0.5 58-60.5°; L-2,2-dimethyl-3-carbobenzyloxy-4-carboxy, isolated as the benzylamine salt, m. 124-8°; D-4-carboxy-5,5-dimethyl, m. 196-7° (decompn.); L-isomer, m. 193-4°; DL-mixt., m. 200-1° (decompn.) [HCl salt, m. 199-200°, or 191-2° (decompn.), according to another group of workers]; 3-acetyl-4-carboxy-5,5-dimethyl, m. 152-5° (Me ester, yellow sirup); 3-chloroacetyl-4-carboxy-5,5-dimethyl, m. 133-5°; DL-3-benzoyl-4-caboxy-5,5-dimethyl, m. 151-2° (Me ester, m. 63-4°, converted by KMnO4 to a sulfone, m. 133-4°); D-3-carbobenzyloxy-4-carboxy-5,5-dimethyl, isolated as the benzylamine salt, m. 140-1°; DL-3-phenylcarbamyl-4-carboxy-5,5-dimethyl, m. 191-2°; 3-[(carbethoxymethyl)carbamyl]-4-carbomethoxy-5,5-dimethyl, m. 80-2°; D-2-cyanomethyl-4-carboxy-5,5-dimethyl, m. 184-5° (decompn.); Me ester-HCl, m. 170-1°, [α]D 97° [free base, m. 78-9°, [α]D 101° (c 1.0, MeOH)]; 4-carboxy-2,5,5-trimethyl, m. 103-5°; 2-isopropyl-4-carboxy, m. 181° (decompn.); 2-methyl-2-ethyl-4-carboxy, m. 132-3° (decompn.) (HCl salt, m. 145-6°); 2-isopropyl-3-carbomethoxy-4-carboxy, m. 88.5-90° (benzylamine salt, m. 149-9.5°); 2-isopropyl-3-carbethoxy-4-carboxy, m. 63.5-4.5° (benzylamine salt, m. 113.5-14.5°); 2-isopropyl-3-carbobenzyloxy-4-carboxy, oil; L-2-acetonyl-4-carboxy, m. 155° (decompn.); L-2-isobutyl-4-carboxy, m. 154° (decompn.); 2-ethyl-4-carboxy-5,5-dimethyl, m. 173-4°; 2-ethyl-3-acetyl-4-carboxy-5,5-dimethyl, m. 152-4°; DL-2-(1,2-dihydroxyethyl)-4-carboxy-5,5-dimethyl, m. 201° (decompn.); DL-4-carbomethoxy-2,2,5,5-tetramethyl, m. 48-9° (HCl salt, m. 162-3°; picrate, m. 150°); D-isomer, b0.1 59°, m. 18-20°, [α]546125 116° (c 1.5, alc.) (HCl salt, m. 143-4°, [α]546127 91° (c 0.95, water)); DL-4-carbethoxy-2,2,5,5-tetramethyl, b0.05 42-5° (HCl salt, m. 167-8°). The following esters of DL-2,2,5,5-tetramethyl-4-thiazolidinecarboxylic acid (XVII) were also prepd.: Pr (HCl salt, m. 160-1°; picrate, m. 137-9°); iso-Pr (HCl salt, m. 169-70°; picrate, m. 149-50°); Bu, b0.1 80° (HCl salt, m. 160°; picrate, m. 132°); iso-Bu (HCl salt, m. 170°; picrate, m. 146-7°); Am (HCl salt, m. about 110°); iso-Am (HCl salt, m. 155-6°); hexyl (HCl-salt, m. 128°; picrate, m. 138°); isohexyl (HCl salt, m. 163°; picrate, m. 130°). Derivs. of XVII: DL-3-formyl, m. 141-2° (Me ester, b0.1 110-15°); 3-Ac (Me ester, m. 57-8°); 3-chloroacetyl, m. 148-9° (decompn.); 3-Bz (Me ester, m. 88-9°); 3-phenylacetyl, m. 159-60°. L-2-Methyl-2-acetonyl-4-carboxythiazolidine, m. 160° (decompn.); however, as subsequent tests and UV data were more in agreement with an open thiol structure, the constitution of this product is doubtful. DL-4-Carboxy-2,2,5-trimethyl-5-ethylthiazolidine-HCl, m. 209-10° (decompn.); DL-2-ethyl-4-carboxy-2,5,5-trimethylthiazolidine, m. 183-3.5° (decompn.); DL-2-propyl-4-carboxy-5,5-dimethylthiazolidine, m. 97-9°; DL-2-iso-Pr isomer, m. 181-2.5° (the Me ester with H2O2 gave the Me

ester of DL-penicillaminic acid, m. 215-19°); D-2-isopropyl-3-benzoyl-4-carboxy-5,5-dimethylthiazolidine, m. 163-4° (Me ester, prepd. with CH2N2); 2-phenyl-4-carbomethoxythiazolidine, b0.5-1 153-5°, nD20 1.5738; L-2-phenyl-3-acetyl-4-carboxythiazolidine, m. 152.5-4°; 2-phenyl-3-benzoyl-4-carboxythiazolidine, m. 153-4°; 2-phenyl-3-phenylacetyl-4-carboxythiazolidine, m. 171-3°; DL-2-isobutyl-4-carboxy-5,5-dimethylthiazolidine, m. 145-7°; L-2-(o-hydroxyphenyl)-4-carboxythiazolidine, m. 167° (decompn.); L-2-hexyl-4-carboxythiazolidine, m. 148-50° (decompn.); L-2-benzyl-4-carboxythiazolidine, m. 165-70°, [α]D21 -90.5° (c 1.0, N HCl); L-2-benzyl-3-carbethoxy-4-carboxythiazolidine, m. 135°; 2-spirocyclohexyl-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m. 200-1°; DL-2-spirocyclohexyl-4-carbomethoxy-5,5-dimethylthiazolidine-HCl, m. 183°; L-2-hexyl-4-carboxy-5,5-dimethylthiazolidine, m. 113-14°; DL-isomer, m. 120-1°; DL-2-hexyl-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m. 139-40°; DL-2-phenyl-4-carboxy-5,5-dimethylthiazolidine, m. 145-6° [HCl salt, m. 172-3° (decompn.)]; DL-2-phenyl-4-carbomethoxy-5,5-dimethylthiazolidine-HCl, m. 154°; DL-2-phenyl-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m. 196-7°; DL-2-phenyl-3-carbobenzyloxy-4-carboxy-5,5-dimethylthiazolidine, m. 145-9°; DL-2-phenyl-3-benzylcarbamyl-4-carbomethoxy-5,5-dimethylthiazolidine, m. 199-203°; D-2-(p-chlorophenyl)-4-carboxy-5,5-dimethylthiazolidine, isolated as the semicryst. Na salt; DL-2-(o-hydroxyphenyl)-4-carboxy-5,5-dimethylthiazolidine, m. 180-1° (decompn.); DL-2-benzyl-4-carboxy-5,5-dimethylthiazolidine, m. 108-10°; DL-II and 2,3-hexanedione gave a product isolated as the HCl salt, m. 161-2° (decompn.); DL-2-spirocyclohexyl-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 219° (decompn.). No satisfactory thiazolidines were prepd. from MeCOPh, Ph2CO, MeCHClCOMe, 3,4-dihydro-1(2H)-Naphthalenone, glucose, benzoin, quinone, Et cyclohexan-1-one-2-carboxylate, Et aminoacetoacetate, MeCH:CHCHO, and CH2:CHCHO; D-2-(α-camphoryl)-4-carboxy-5,5-dimethylthiazolidine, m. 175°; L-2-diethoxymethyl-4-carboxythiazolidine, m. 149° (decompn.); DL-2-diethoxymethyl-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 99-101° (another fraction of the same compn. m. 126-7°); DL-2-(3-methoxy-4-acetoxyphenyl)-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m. 199°; DL-2-(o-acetoxyphenyl)-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m. 203-4°. Dicarboxythiazolidine derivs.: L-2,4-Dicarboxy, m. 184-5°; D-2-carbobutoxy-4-carboxy-5,5-dimethyl, m. 141-2°; D-2-carboxy-4-carbomethoxy-5,5-dimethyl, isolated as the Ba salt (benzylamine salt, m. 156-7°); D-2-carboxy-3-nitroso-4-carbomethoxy-5,5-dimethyl, m. 96-9° (benzylamine salt, m. 152-3°); D-2-carbobutoxy-3-nitroso-4-carboxy-5,5-dimethyl, isolated as the benzylamine salt, m. 134-5°; L-2-carbethoxymethyl-4-carbethoxy, b0.1 115-17°; DL-2,4-dicarboxy-2,5,5-trimethyl, m. 174° (decompn.); L-2-methyl-2-carbethoxymethyl-4-carbomethoxy, b0.55 118-21°, nD20 1.4952; D-2-carbethoxymethyl-4-carboxy-5,5-dimethyl, m. 152-4°, [α]D23 122.5° (c 0.392, MeOH) (HCl salt, m. 128-38°); D-2-carbethoxymethyl-4-carbomethoxy-5,5-dimethyl [HCl salt, m. 167-9°, [α]D23 78° (c 0.94, MeOH)]; D-2-carboxymethyl-4-carbomethoxy-5,5-dimethyl, m. 100-5°; D-2-carbomethoxymethyl-4-carbomethoxy-5,5-dimethyl (HCl salt, m. 147-9°); D-2-carbethoxymethyl-3-methoxalyl-4-carboxy-5,5-dimethyl, m. 128-30°; D-2-carbethoxymethyl-3,4-dicarbomethoxy-5,5-dimethyl, b0.15 160°; L-2-cyanomethyl-3-acetyl-4-carbomethoxy-5,5-dimethyl, m. 112-13°; D-2-carbethoxychloromethyl-4-carboxy-5,5-dimethyl, m. 114-15° (decompn.); D-2-carbethoxymethyl-4-carboxy-2,5,5-trimethyl,

m. 153-4°; DL-isomer, m. 176-7°; DL-2-carbamylmethyl-4-carboxy-2,5,5-trimethyl, m. 199-200°; L-2-(phenylcarbethoxymethyl)-4-carboxy, m. 163-4°; L-2-(phenylcarboxymethyl)-4-carboxy, m. 165°; L-2-(phenylcarbethoxymethyl)-4-carbomethoxy, m. 60-1°; L-2-(phenylcarbethoxymethyl)-4-carbethoxy, m. 57-8° (HCl salt, m. 125-6°); L-2-(phenylcyanomethyl)-4-carboxy, m. 159-60° (decompn.) (Et ester-HCl). Amino monocarboxythiazolidine derivs.: L-2-Aminomethyl-4-carbethoxy (di-HCl salt, m. 145-6°); L-2-(benzylaminomethyl)-4-carboxy, m. 208-10° (decompn.); L-2-(carbethoxyaminomethyl)-4-carboxy, m. 158°; L-2-(carbethoxyaminomethyl)-3-phenylacetyl-4-carboxy, m. 198° (decompn.); DL-2-aminomethyl-4-carbomethoxy-5,5-dimethyl (di-HCl salt, m. 161-2°); DL-2-aminomethyl-4-carboxy-5,5-dimethyl, m. 200° [di-HCl salt, m. 200-1° (decompn.)]; DL-2-aminomethyl-4-carbethoxy-5,5-dimethyl [picrate, m. 169-70°]; [di-HCl salt, m. 167-8° (decompn.)]; DL-2-(carbethoxyaminomethyl)-4-carboxy-5,5-dimethyl (HCl salt, m. 183°); 2-(benzamidocarboxymethyl), m. 108-11°; 2-(benzamidocarboxymethyl)-3-isobutyryl, m. 201°; 2-[(α-phenylacetamido)-carbomethoxymethyl], m. 108-11° [HCl salt, m. 172-3° (decompn.)]; DL-2-(p-tolylsulfonamidomethyl)-4-carboxy-5,5-dimethyl [HCl salt, m. 175° (decompn.)], from DL-II.HCl and p-MeC6H4SO2NHCH2CH(OEt)2, m. 67°; the latter gave a dinitrophenylhydrazone, m. 175°; the thiazolidine deriv. formed a Me ester-HCl, m. 188-90° (decompn.). p-AcNHC6H4SO2Cl converted DL-isopropylidenepenicillamine-HCl to the diketopiperazine, m. 210-12°; β-MeCH(NH2)CH2CH(OEt)2.HCl, m. 113°, was converted to β-(caproylamino)butyraldehyde di-Et acetal, b0.025 150°, nD22 1.4475 (dinitrophenylhydrazone, m. 154°); β-(α-phenylacetamido)butyraldehyde di-Et acetal, b0.007 160-2°, nD22 1.5130 (2,4-dinitrophenylhydrazone, m. 184°); DL-2-(2-aminopropyl)-4-carboxy-5,5-dimethylthiazolidine-2HCl, m. 201° (decompn.); β-(caproylamino)propionaldehyde di-Et acetal, b0.07 132° (dinitrophenylhydrazone, m. 154-5°); DL-2-(2-caproylaminoethyl)-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 186° (decompn.). Amino dicarboxythiazolidine derivs.: L-2-(Formamidocarbethoxymethyl)-4-carboxy (HCl salt, m. 185° (decompn.)); Et ester of the free base, m. 109°; D-2-(aminocarbomethoxymethyl)-4-carbomethoxy-5,5-dimethyl, b0.001 100°; nD24 1.5119; the DL-compd. HCl salt, hygroscopic powder; DL-2-(aminocarboxymethyl)-4-carboxy-5,5-dimethyl mono-Ba and mono-Na salts were prepd.; DL-2-(aminocarbethoxymethyl)-4-carboxy-5,5-dimethyl [di-HCl salt, m. 72-5° (decompn.)]; D-2-(aminocarbethoxymethyl)-4-carbethoxy-5,5-dimethyl, purified by evaporative distn. at 0.003 mm. and 100°, [α]D 35° (c 0.3, EtOH); D-2-(aminocarbethoxymethyl)-3-phenylacetyl-4-carboxy-5,5-dimethyl (HCl salt, m. 118-20°); D-(2-aminocarbethoxymethyl)-3-phenylacetyl-4-carbomethoxy-5,5-dimethyl (HCl salt, m. 151-3°); the corresponding dicarboxylic acid HCl salt, m. 156-8°. MeI and 2-(aminocarbomethoxymethyl)-4-carbomethoxy-5,5-dimethyl refluxed for 20 h. gave a red oil. Tricarboxythiazolidine derivs.: D-2,2-Dicarbethoxy-4-carboxy-5,5-dimethyl (HCl salt, m. 151-2° (decompn.)); DL-2-carbethoxy-2-carbethoxymethyl-4-carboxy-5,5-dimethyl, m. 148-9°; Thiazolidines with linked and fused heterocyclic substituents: 2-(2-Furyl)-DL-4-carboxy-5,5-dimethylthiazolidine, m. 141-3° (decompn.); 4,3,2',3'(D-4'-carbomethoxy-5',5'-dimethylthiazolido)-2-imidazolidone, m. 128-9°; DL-compd., m. 124-5°; 4,3,2',3'(D-4'-carbomethoxy-5',5'-dimethylthiazolido)-5-carbomethoxy-2-imidazolidone, m. 168-9° (decompn.); 1-benzyl-2-phenyl-3,4,3',2'-(4'-carboxythiazolido)imidazolidine, m.

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163°; 3,4,3',4'-(2'-benzylthiazolido)-1-phenylhydantoin, m. 91-2°; 3-(carbethoxymethylcarbamyl)-4-carbomethoxy-5,5-dimethylthiazolidine, m. 80-2°; 1-carboxymethyl-3,4,3',4'-(5',5' dimethylthiazolido)hydantoin, m. 151-2°; Addnl. information in printed abstr.

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GI For diagram(s), see printed CA Issue.
AB A series of indole derivs., o-C6H4.CR:CR'.NH (I), related to gramine, is prepared, by the Mannich reaction. Reduction of o-O2NC6H4CH2COCO2H, prepared according to DiCarlo (C.A. 38, 5218.1), with Na2S2O4 gives the indolecarboxylic acid which, refluxed with EtOH, gives 90% Et ester (II), m. 119-20°. Dropwise addition over a period of 2 h. of 24 g. EtCHO to 64 g. Et2NCH2CH2CH2CH(NH2) Me at 0° with stirring, adding a small amount of KOH, keeping the mixture 1 h., drying the organic layer over KOH, keeping it overnight in a refrigerator, and distilling over NaOH give the aldimine, b34-35 124-8°, which, hydrogenated at 3 atmospheric with 5% Pd-charcoal, gives 68% Et2NCH2CH2CH2CH(NHPr)Me (III), b30-32 128-35°, b. 234-6° (di-HCl salt, slightly hygroscopic crystals, m. 219.5-20.5°). I are obtained by treating the appropriate indole derivative in AcOH with a 10% excess of NHR2 and then with 37% HCHO according to the procedure used by Kuhn and Stein (C.A. 31, 3913.9) for the synthesis of gramine. The mixture is diluted with H2O, washed with ether, made alkaline, and the precipitate is recrystd. In this way the following I are prepared (R, R', yield, and m. p. in the order given): Me(PhCH2)NCH2, H, 90%, 114°; MePhNCH2, H, 7%, 126-7°; (CH2:CHCH2)2NCH2.H, 60%, 77.5-8°; CH2.(CH2)4.NCH2, Me, 79%, 156-7°; CH2.CH2.O.CH2.CH2.NCH2, Me, 92%, 175-6°; Pr[Et2N(CH2)3CHMe]NCH2, CO2Et, 80%, 78-9°; Me-(PhCH2)NCH2, CO2Et, 93%, 104-5°; CH2.CH2.O.CH2.CH2.NCH2, CO2Et, 94%, 152-3°; (CH2:CHCH2)2NCH2, CO2Et, 88%, m. 100-1°; Pr2NCH2, CO2Et, 94%, 78-9°; (HOCH2CH2)2NCH2, CO2Et, 70%, m. 105-7°; Me2NCH2, CO2Et, 83%, m. 86-7°.

ACCESSION NUMBER: 1950:49315 CAPLUS
DOCUMENT NUMBER: 44:49315
ORIGINAL REFERENCE NO.: 44:9409a-e
TITLE: The preparation of Mannich bases related to gramine
AUTHOR(S): Brehm, Warren J.; Lindwall, H. G.
CORPORATE SOURCE: New York Univ.
SOURCE: Journal of Organic Chemistry (1950), 15, 685-7
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 43 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 31, 3888.2. The condensation of CH2O and alkoxyphenylalkylamines in the presence of acid gave mixts. of low-polymeric bases which could be partially separated into their constituents. Polymers with 3-4 residues of the parent amine joined by CH2 groups between the rings had a pronounced and enduring effect in lowering blood pressure, the presence or absence of HOCH2 groups (presumably attached to terminal rings) not being critical Standard prepns.: Slow addition of 5.85 cc. formalin solution to 12.4 g. 4-MeOC6H4CH2CH2NHMe (I) in 15 cc. H2O at 0-5°, then 30 cc. cold concentrated HCl (final concentration 6 N), and heating on the steam bath x hrs. gave GC-142-x; x generally was 4 h., GC-142-4 being more potent than GC-142-1 and -2. A minor variation was Et2O extraction of the mixture before addition of the HCl. The solution was then concentrated on the steam bath in vacuo, the residue dissolved in 40 cc. absolute EtOH, 1 volume EtOAc added, and the jelly, formed by 16 h. cooling, converted by 2 vols. Et2O to a granular precipitate, which was filtered rapidly, washed with anhydrous Et2O, and dried in vacuo. Other prepns. were M-25, from 3,4-(MeO)2C6H3CH2CH2NHMe, M-27 from the 2,3-analog, GD-6 from hordenine, M-96 from hordenine Me ether (II), M-118 from II.MeCl, M-114 from 2-MeOC6H4CH2CH2NMe2, GC-114 from 4-MeOC6H4CH2NHMe, GC-104-II from o-anisidine, and GC-110, the quaternary salt prepared by methylation of GC-104-II with MeI in MeOH and Na2CO3. Isolation of dimers: GC-60 was prepared by addition of 3 cc. formalin and 20 cc. 20% HClO4 in the cold to 6.4 g. I, heating 2 h. in the steam bath, chilling, and crystallization of the gummy solid twice from H2O to 3.7 g. colorless microcryst. salt, converted to the base, then to the HCl salt, m. 261-2° (from EtOH-Et2O). The free base was distilled at 0.4 μ and 125-30° bath temperature, giving a product of mol. weight 329 (342 calculated for C21H30N2O2), again converted to the HCl salt, m. 264-5°. GC-55: 3,4-Me(MeO)C6H3CH2CH2NMe2 (III), CH2O, and HCl gave a poor yield of impure dimer HCl salt, m. 221-2°, and much higher polymers. GC-125-1 and -II were formed in the attempted preparation of a trimer; 4 g. formalin, 9.65 g. III, and 48 g. concentrated HCl were treated 2 h. at 30-40° with a current of HCl gas, the mixture concentrated in vacuo, the residue (mostly monochloromethyl derivative ?) treated with 5.4 g. 4-MeOC6H4CH2CH2NMe2 and 10 cc. concentrated HCl 7 h. on the steam bath, concentrated in vacuo, and the residue made alkaline in H2O; Et2O extraction gave GC-125-I, Et2O-soluble, 520 mol. weight (Rast), and GC-125-II, Et2O-insol. and EtOAc-soluble Distillation at 0.3 μ to 130° of 275 mg. GC-114 gave 115 mg. distillate of mol. weight 244 (314 for dimer) and 140 mg. residue, 496 mol. weight (477 for trimer). The best fractionation of polymers was with the Craig counter-current distribution method (C.A. 41, 6172a). M-96 was largely freed of dimer (about 25%) by partial basification of the aqueous solution and solvent extraction, leaving 70% GC-81-II. Distribution of two 1-g. portions of this in 9 separatory tubes between 120 cc. each of 50-50 C6H6-hexane and 75% aqueous MeOH in each tube, and conn. gave a total of 1.4 g. residue (IV) in tubes 0-4 and a sep. hydrophilic component (V) in tubes 7-8. IV showed homogeneity on further distribution, and 2 fractions,

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tested as GC-131-2 and-3, were converted to HCl salts, the former giving no CH4 (Zerewitinoff). V from 3 runs (490 mg.) on redistribution gave 185 mg., GC-132-8, analyzing C37H55N3O5 (trimer with 2 HOCH2 groups), contg. 2 active H atoms (1.12 cc. CH4 found, 1.07 calcd. for mol. wt. of 621). Distn. of 0.1 g. free base, at 0.2 μ and 175°, gave 40 mg. (mol. wt. 296), 25 mg. at 208° (mol. wt. 572 found, 561 calcd. for trimer), and 25 mg. residue (557). Terminal fractions (655 mg.) from several large distributions were redistributed between 50-50 C6H6-hexane and 55% aq. MeOH, giving in tube 0 135 mg., 746 mol. wt. in camphor (782 calcd. for tetramer with 1 HOCH2 group), and 0.61 cc. CH4 (0.80 cc. calcd.)(Zerewitinoff). The contents of tube 8 (90 mg.) gave a mol. wt. of 567 in borneol (612 with depression of m.p. in lit. 35.6° against 33° obsd.; 621 calcd. for trimer with 2 HOCH2 groups), and 1.57 cc. CH4 (1.85 calcd.). No active fraction gave cryst. salts and the phys. properties and anal. data indicated that sepn. had been between types only, not species. GC-114 and the polymer from 4-MeOC6H4CH2NMe2 were less potent and more toxic than others; the % dimer was higher and d.p. lower, anticipated with a cationic group only one stage removed from the C6H6 ring. The high potency of GC-110 in contrast with GC-104 II showed the dependence of activity on the presence of groups that would be cationic under physiol. conditions. Expts. on a trimer contg. 2 or 3 properly spaced cationic groups, which should give strong depressor action, are under way. Pharmacol. data on the above compds. will be reported elsewhere. A structure with crosslinking between N atoms by CH2O was eliminated when M-96 and M-118 both showed max. potency, so CH2 links between arom. nuclei seem more probable, as shown in VI, Z and Z' being H, CH2OH, or CH2Cl groups.

ACCESSION NUMBER: 1949:36537 CAPLUS
DOCUMENT NUMBER: 43:36537
ORIGINAL REFERENCE NO.: 43:6593h-i,6594a-i,6595a-c
TITLE: A family of long-acting depressors
AUTHOR(S): Baltzly, Richard; Buck, Johannes S.; De Beer, Edwin J.; Webb, Frederick J.
SOURCE: Journal of the American Chemical Society (1949), 71, 1301-5
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 44 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB It is proposed that CO(NH2)2 reacts with HCHO as an amino acid amide; in such a mol., the amide-NH2 would react with HCHO to yield a methylenimine derivative which would trimerize to a cyclic trimethylenetriamine compound and the amide-NH2 would react to yield methylenebisamide links between the rings. The resulting polymer would be a highly cross-linked structure. H2NCH2CONH2.HCl (1 mol) and 2 mol HCHO in aqueous solution at pH 4.2 (NaOH) at room temperature, the H2O being removed in a desiccator over P2O5, give a brittle polymer, C21H36N12O6, decomps. about 200°; gelation occurs only when 1.5 or 2 mol HCHO are present; the reaction is twice as fast with 1.5 as with 2 mol of HCHO; gelation does not occur in solns. of pH less than 3.2 or of 5 or higher; at 0°, a solution of pH 4.2 gelled during several weeks to yield a very soft, opaque material; at 60° no gelation is observed The preparation of H2N(CH2)5CO2Et (I) (52%) from the HCl salt (96% from ε-aminocaprolactam) is described. I (25 g.) and 275 cc. concentrated NH4OH, shaken for 60 h., give 63% of ε-aminocaproamide (II), m. 50-1°, very hygroscopic and absorbs CO2 from the air. II (1 mol) and 2 mol aqueous HCHO evolve heat on being mixed; a semisolid gel is formed in about 1 h. and a product resembling "art gum" after 4 days; the yield of the polymer, C15H28N4O2, decomposing 185°, is 97.5% (based on 1.5 CH2 units per amide unit); H2NCH2CO2Et (21 g.) and 280 cc. 35% aqueous MeNH2 shaken for 60 h., the excess MeNH2 removed at 40°, the H2O removed by distillation with C6H6 at 30°, the residue in 20 cc. H2O treated with 25 cc. concentrated HCl and 400 cc. absolute EtOH, give 60% of glycine methylamide-HCl (III), m. 153.5-6°. III (1.25 g.) and 0.77 cc. HCHO, made slightly alkaline with NaOH and heated at 60° for 4 h., give 12% of the polymer, (C4H8N2O3)3, m. 167.5-9° (purification described). MeNHCH2CONH2 (1 mol) and 2 mol HCHO, acidified with 2 drops concentrated HCl, heated at 60° for 4 h., give an amber glass (viscous liquid in air), C4H9ON2Cl; this is probably a linear polymer of a low mol. weight AcNHCONH2 does not react with HCHO in neutral or basic solution; heated in an acid solution at 70° for 4 h., they give a resinous material, m. 245-6° (34.45% N); another preparation m. 275-8.5° (decomposition), 28.7% N. H2NCO2Et (89 g.) and 93 cc. HCHO with 25 mL. concentrated HCl, refluxed 5 h., give 95-100% of EtO2CN.CH2.N(CO2Et).CH2.N(CO2Et).CH2, m. 101-2°; the EtO groups could not be replaced by NH2 groups.
ACCESSION NUMBER: 1946:37225 CAPLUS
DOCUMENT NUMBER: 40:37225
ORIGINAL REFERENCE NO.: 40:7166d-i,7167a
TITLE: Structure of urea-formaldehyde resins
AUTHOR(S): Marvel, C. S.; Elliott, J. R.; Boettner, Fred E.; Yuska, Henry
CORPORATE SOURCE: Univ. of Illinois, Urbana
SOURCE: Journal of the American Chemical Society (1946), 68, 1681-6
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 45 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB The structural analogy between formaldehyde hydrate, HOCH2OH, and R2NCH2NR2 (I) (R = H or organic radical) is validated by expts. in which HCHO and I are interchangeably used in reactions which are characteristic of the former. In each reaction studied, both reagents lead to the formation of the same chief product, the byproduct of the reactions with I being the liberated amine corresponding to the H2O formed when HCHO is used. The following I are used: methylenebis-p-toluidine (II), -p-chloroaniline (III), -p-bromoaniline (IV), -p-anisidine (V), -ethylaniline (VI), -piperidine (VII), and -morpholine (VIII); the last 3, having no amino H, are NH3 analogs of formaldehyde acetals. In some expts. the trimeric methylene-p-toluidine (IX) is used, giving the same products as obtained from II. The reaction may in some cases be reversible but no investigation is carried out in this regard. II, m. 93.5-5°, III, m. 64-6°, IV, m. 90-2°, and V, m. 63-5°, are prepared according to Bischoff and Reinfeld (Ber. 36, 41(1903)); VI, m. 74-5°, according to v. Braun (C. A. 2, 2804); VII, b2 69-72°, in 90% yield, and VIII, b2 99-107°, in 69% yield, according to Ehrenberg (J. prakt. Chemical 36, 117(1887)). The following anthranilanilides are prepared by interaction of the corresponding amines and isatoic anhydride: N-phenyl- (X), m. 128.5-9°, N-p-bromophenyl- (XI), m. 154-5°, and N-p-anisylanthranilamide (XII), m. 123-3.7°. Reaction of 0.01 mol. N-(6-amino-α1-m-xylyl)p-toluidine and 0.01 mol. II, III, IV, V, VI, VII or VIII by refluxing in 50-90 cc. absolute EtOH for 1 h. gives 3-p-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (XIII), m. 139-41°, and the corresponding amines in the following yields: with II, 97% XIII and 86% p-MeC6H1NH2 (Bz derivative m. 152-3°); with III, 76% and 86% p-ClC6H4NH2 (Bz derivative m. 188°); with IV, 77% and 84% p-BrC6H4NH2 (Bz derivative m. 201°); with V, 70% and 99% p-MeOC6H4NH2 (Bz derivative m. 154.5-5°); with VI, 95%; with VII 95% and 99% piperidine (HCl salt m. 242.5-4°); with VIII, 88% and 73% morpholine (HCl salt m. 168-72°); and with VIII in the presence of EtONa, 25%. An experiment carried out with VII in the complete absence of moisture gives 92% XIII and 100% piperidine. XIII prepared with HCHO m. 139-41°. X (0.01 mol.) dissolved in 10-20 cc. EtOH containing NaOH and 2-5 cc. 37% HCHO, when warmed to 60° and chilled, gives 96% 3-phenyl-1,2-dihydro-4(3)-quinazolone (XIV), m. 176° or 180° (corrected). XI under the same conditions gives 82% 3-p-bromophenyl derivative (XV), m. 194-5° or 199-200° (corrected), and XII gives 91% 3-p-methoxyphenyl derivative (XVI), m. 185-5.5°. When X is treated with HCHO in alkaline EtOH at room temperature, 1-(hydroxymethyl)-3-phenyl-1,2-dihydro-4(3)-quinazolone (XVII), m. 109-10° or 110-11° (corrected, decomposition) is formed. It solidifies and remelts 172-5° after formation of XIV. When a solution of XVII in absolute EtOH is distilled, HCHO is liberated, identified as methylenadimethone, m. 190-1°, and XIV is formed. Interaction of o-NH2C6H4CONH2 with HCHO in alkaline EtOH gives a compound (XVIII) m. 141°, in the absence of alkali, a product m. 65-70° with evolution of HCHO, resolidifying and subliming around 170°. XVIII when heated with H2O or NH4OH gives HCHO. Acidification of the solution of XVIII in NH4OH with AcOH and treatment of the filtrate with Thatcher's reagent gives urotropine tetraiodide, m. 210° after darkening at 110-15° and shrinking at 165-70°. Mild oxidation of XVIII with KMnO4 in Me2CO gives 4(3)-quinazolone, m. 210-14° (picrate m. 206-8°), indicating that XVIII is 1,3-bis(hydroxymethyl)-1,2-dihydro-4(3)-quinazolone. The formation of XIV, XV and XVI by ring closure of X, XI and XII with II-VIII is studied under various conditions given, together with the results, in a table. The structure of XIV, XV

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and XVI is proved by oxidn. with KMnO4 in 10% excess of the calcd. amt. in dry Me2CO at 0°, with XIV giving 48% 3-phenyl-4(3)-quinazolone, m. 138-9° (picrate m. 177-8°), XV giving 36% 3-p-bromophenyl-4(3)-quinazolone, m. 189-90° (picrate m. 171-3°), and XVI giving 87% 3-p-methoxyphenyl-4(3)-quinazolone, m. 193.5-4°. The latter is synthesized in 28% yield by heating o-NH2C6H4CO2H and formyl-p-anisidine at 150° for 1.5 h. When 0.02 mol. 1-naphthol (XIX), 2-naphthol (XX), or carvacrol (XXI) and 0.02 mol. II, III, or VII in 20 cc. abs. EtOH are refluxed for 15-60 min., the following (aminomethyl)phenols are formed: XIX and VII give 77% 2-(1-piperidylmethyl)-1-naphthol, m. 133.5-4.5°, XX and VII give 97% 1-(1-piperidylmethyl)-2-naphthol, m. 95-6.5° (under anhyd. conditions with ligroin (b. 90-120°) as solvent the yield is 61%), XX and II give 80% 1-(p-toluinomethyl)-2-naphthol (XXII), m. 136.5-7°, XX and III give 81% 1-(p-chloroanilinomethyl)-2-naphthol, m. 139-41.5°, and XXI and VII give 24% (1-piperidylmethyl)carvacrol, m. 182-3°. XXII dissolves in 10% NaOH on heating and from the soln. XXII is recovered unchanged on acidification, indicating that its p-(toluinomethyl) group is not attached to the OH group and that its phenolic character is relatively weak. When XX and IX are heated in EtOH in the presence of EtONa, 52% 1,1'-methylenedi-2-naphthol (XXIII), m. 194-5°, is obtained. In the absence of EtONa 59% XXII, 22% XXIII, some unchanged XX and 80% p-MeC6H4NH2.HCl can be isolated. When a mixt. of 0.03 mol. PhNMe2 and 0.01 mol. VII is satd. with HCl, the solid dissolved in hot abs. EtOH and refluxed for several hrs., 22% bis(p-dimethylaminophenyl)methane, m. 88-90°, is formed. Carbazole (XXIV) and HCHO in hot glacial AcOH or with VII in the presence of Ac2O give methylenedicarbazole, m. 301-3°, in 52 and 77% yield, resp. When, however, XXIV and HCHO are refluxed in 85% EtOH in the presence of piperidine, 99% 9-(1-piperidylmethyl)carbazole (XXV), m. 99-9.5°, is obtained. XXV is also formed on heating of a mixt. of 0.02 mol. XXIV with 0.01 mol. VII for 1 h. at 180-5°. The analogy between HOCH2OH and I is further demonstrated by the formation of (aminomethyl)imides by interaction of phthalimide (XXVI), piperidine and HCHO. On heating of an equimol. mixt. of XXVI, HCHO, and piperidine in 80% EtOH, or on refluxing of a soln. of 0.02 mol. XXVI and 0.02 mol. VII in 20 cc. EtOH for 2 h., N-(1-piperidylmethyl)phthalimide, m. 119-19.5°, is obtained in 95 and 92% yield, resp. Under the same conditions succinimide (XXVII), piperidine and HCHO or XXVII and VII give N-(1-piperidylmethyl)succinimide, m. 107-7.5°, in 46 and 89% yield, resp. Dimethyldihydroresorcinol (XXVIII) used as reagent for aldehydes also reacts with the I. By dissolving 0.01 mol. XXVIII and 0.005 mol. I in 10-15 cc. EtOH or Bu2O with minimal warming, the following yields of methylenedimethone, m. 188-9°, are obtained from the various I: from II in EtOH 93%, in Bu2O 97%; from III in EtOH 99-100%, in Bu2O 96-100%; from IV in Bu2O 96%; and from V in Bu2O 58-78%.
ACCESSION NUMBER: 1942:12323 CAPLUS
DOCUMENT NUMBER: 36:12323
ORIGINAL REFERENCE NO.: 36:1938b-i,1939a-h
TITLE: Some reactions of methylenebisamines as ammono aldehydes
AUTHOR(S): Feldman, J. R.; Wagner, E. C.
SOURCE: Journal of Organic Chemistry (1942), 7, 31-47
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 46 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB The course of the condensation of CH2O with PhNH2 and p-MeC6H4NH2 depends entirely on the ionic condition of the medium in which the condensation takes place. Thus, methylenediaryldiimines, CH2(NHAr)2, (I), are formed at the concns. [H+] < 1 + 10-7, while tertiary bases, ArN:CH2 (II), at [H+] ≥ 1 + 10-7. This change in the character of condensation products appears quite sharply and is already marked within the limits of H-ion concentration of 1-2 pH. In both cases the one base becomes contaminated with the other; thus, II formed at pH 7 contains some I, and I formed at pH > 7 contains II. These admixts. of the other base are very small and become smaller for the condensation with the greater deviation of H-ion concentration from the value pH 7. In the condensation in the medium [H+] > 1 + 10-7 near the value pH 7 the admixt. of I generally disappears. This fact is explained by the instability of I in media with an acid concentration of H ions. I is changed to II under H2O and on boiling with alc. with the separation of ArNH2 (Ann. 302, 335). These transformations proceed more rapidly with the higher H-ion concentration and the higher temperature Contrary to Eibner (Ber. 30, 1448), the proportions of the reacting CH2O and arylamines do not affect the course of condensation. I is as easily obtained with a double excess of CH2O in a medium [H+] < 1 + 10-7 as with the theoretical amount of CH2O. It follows that the scheme of the formation of II by Eibner is incorrect, and I is not formed as an intermediate product in the preparation of II, because the reaction CH2(NHAr)2 + CH2O → 2ArN:CH2 + H2O is impossible in the medium [H+] < 1 + 10-7, while the formation of I with an excess of an amine is impossible with good distilled H2O with [H+] near 1 + 10-7, for under these conditions II is formed. CH2(NHC6H4Me-p)2 is obtained in 80-90% yield by interaction of 0.05 mole of CH2O (30%) and 0.1 mole of p-MeC6H4NH2 in 100 cc. of H2O or a buffer solution with [H+] = 1 + 10-8; the filter cake, dried and recrystd. from dilute alc., m. 89°. Condensation at [H+] = 1 + 109 gives a pure product after 1 crystallization Identical results are obtained by using an excess of CH2O, CH2:NC6H4Me-p is obtained in 80% yield as above from 1 mole of CH2O and 1 mole of p-MeC6H4NH2 in H2O or buffer solution with [H+] = 1 + 10-7. CH2(NHPh)2, m. 64-5°, is obtained from 0.1 mole of PhNH2 and 0.05 mole of CH2O in H2O or buffer solution with [H+] < 1 + 10-7. CH2:NPh, prepared from 0.1 mole of PhNH2 and 1 mole of CH2O in 200 cc. of H2O with [H+] ≥ 1 + 10-7, m. 140° and 200°. Conversion of CH2(NHC6H4Me-p)2 to CH2:NC6H4Me-p.-CH2(NHC6H4Me-p)2 (1.5 g.), m. 89-90°, pulverized and allowed to stand 4 hrs. at room temperature in 40 cc. of H2O with [H+] = 1 < 10-4, then filtered, washed with H2O and recrystd. from alc., gives a mixture, m. 129-30° and 200°. The conversion can be accelerated with an increase of temperature and the concentration of H ions.
ACCESSION NUMBER: 1932:51374 CAPLUS
DOCUMENT NUMBER: 26:51374
ORIGINAL REFERENCE NO.: 26:5293c-i
TITLE: Condensation of formaldehyde with aromatic amines
AUTHOR(S): Drozdov, N. S.
SOURCE: Zhurnal Obshchei Khimii (1931), 1, 1171-6
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal

L7 ANSWER 46 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
LANGUAGE: Unavailable

L7 ANSWER 47 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB cf. C. A., 8, 127. In attempting to methylate the 2 compds. (I) and (II) with HCHO (Leuckhardt, Ber., 22, 1851, and earlier papers; Eschweiler, Ber., 38, 880), not only was a Me group introduced but the CHOH group was oxidized quant. to C:O; the reaction is general, AcMe being formed when iso-PrOH is heated with HCHO and NHEt2 or piperidine. Thus, 5.6 g. (I) in 10 cc. H2O acidified with conc. HCl, when heated 4 hrs. at 115-20° with 5 cc. of 40% HCHO, gave 5.4 g. 1-α- N-**methylpyrrolidylpropane**-1-one (III). b14 69-74°, b21 80-2°, very hygroscopic, has an unpleasant, strongly basic and narcotic odor, slowly turns yellowish in the light in corked vessels; its superheated vapors color a fir splinter moistened with HCl red; it is stable towards KMnO4 in H2SO4, at once decomposed by alks., at once gives a Ag mirror with a drop of concentrate AgNO3 and at once ppts. Au from neutral AuCl3 solution while from its aqueous HCl solution AuCl3 ppts. the chloroaurate in yellow microscopic needles, m. 106° (corrected). The base is volatile with steam and can be **distilled** under atmospheric pressure. Oxime, b14 140°; picrate of the oxime, reddish brown syrup. Picrate of (I), long yellow needles, sinters about 95°, m. 103° (corrected). In the prepare of (II), a much more effective Pt sponge is obtained when, after the decantation with **distilled** H2O to disappearance of the Cl reaction, it is washed with the solvent to be used in the reduction. If it is filtered off, at once transferred to the vacuum desiccator and dried and air then admitted to the desiccator, it always warms up and cakes, its efficiency being thus decreased. With 0.5 g. of the sponge prepared in the new way, 3.60 g. of pyrrole base absorbed 1166 cc. H (15-7°, 756 mm.) in 16 hrs.; calculate, 1254.2 cc. (0°, 760 mm.). With Pd, the reduction is not confined to the pyrrole nucleus but extends to the side chain, giving a mixture of (II) and 1-α-pyrrolidylpropane, b765 145-50°, has a piperidine-like, strong narcotic odor. From 2.5 g. of (II) in 5 cc. acidified H2O heated 4 hrs. at 115-20° with 6 cc. of 40% HCHO is obtained 2 g. of 1-α- N-**methylpyrrolidylpropane**-2-one (synthetic dl-hygrine), b14 79-83°. b21-2 89-92°, can be kept for weeks in corked tubes without change; its Superheated vapor gives a red color with a fir splinter moistened with HCl while its aqueous HCl solns. are without action; it has a piperidine-like odor, is stable towards KMnO4 in dilute H2SO4, at once decomposed by alks., at once gives Ag2O with AgNO3 and a mirror on warming, can be **distilled** under atmospheric pressure. Picrate, yellow needles, begins to sinter 162°, m. 174° (corrected). Liebermann (Ber., 22, 677) gives 148° as the m. p. of the picrate of natural hygrine. A purer sample of the hygrine (L., Ber., 28, 579) was found by H. to b11-2 79-81°, [α]D20 1.2°, but still gave too high values for N (10.54%; calculate, 9.93) and gave a picrate m. 158° (corrected). Oxime of (IV). m. 125° (corrected); L. (Ber., 26, 852) gives 116-20° for the oxime of natural hygrine. H2NCMe2CH2Ac, b0.14 25° without decompose, is reduced in 1-2 hrs. by alc. and 3-4 times the calculate amount of Na to H2NCMe2CH2CHMeOH, b16 70-5°. 5.7 g. of which, heated 4 hrs. at 115-20° in 10 cc. acidified H2O with 13 cc. of 40% HCHO, gives 4 5-5.0 g. of **diacetonemethylamine**, MeNHCMe2CH2Ac. b15 50-3°, has a menthol-like odor and produces dizziness and headache when inhaled deeply.
ACCESSION NUMBER: 1914:6107 CAPLUS
DOCUMENT NUMBER: 8:6107
ORIGINAL REFERENCE NO.: 8:934e-i,935a-e
TITLE: Synthesis of hygrine. If. Synthesis of the racemic hygrine. A new oxidation method. Further communications on the catalytic reduction of pyrrole

L7 ANSWER 47 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
derivatives
AUTHOR(S): Hess, Kurt
CORPORATE SOURCE: Univ. Berlin
SOURCE: Ber. (1914), 46, 4104-15
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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=>  d his

     (FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005)

     FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005
L1             1 S FORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005
L2         61794 S 50-00-0/RN
L3        166261 S N-METHYL?
L4       1415128 S ?AMINE
L5           889 S L2 AND L3 AND L4
L6        362618 S DISTILL?
L7            47 S L5 AND L6

=> s formaldehyde
          135103 FORMALDEHYDE
             371 FORMALDEHYDES
L8        135208 FORMALDEHYDE
                 (FORMALDEHYDE OR FORMALDEHYDES)

=> s l8 and l2
L9         53548 L8 AND L2

=> s l8 or l2
L10       143454 L8 OR L2

=> s l10 and l3
L11        3718 L10 AND L3

=> s l11 and l4
L12        2315 L11 AND L4

=> s l12 not l7
L13        2268 L12 NOT L7

=> s l13 and l6
L14          36 L13 AND L6

=> d l14 1-36 abs ibib
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L14 ANSWER 1 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

AB The polyamines, useful as intermediates for the manufacture of isocyanates, are
manufactured by (a) reacting PhNH2 with HCHO at resp. mol. ratio 1:(1.5-20) in
acidic ionic liquid, (b) removing the ionic liquid from the reaction mixture and
(c) recycling the ionic liquid to the reaction stage. Thus, adding HCHO (32% solution) dropwise to PhNH2 (PhNH2/HCHO mol. ratio 3.0) at 80°, removing the H2O by azeotropic distillation at 80° in vacuo and heating the reaction mixture at 80-120°/100 mbar gave a precondensate. This was diluted with PhNH2, added dropwise over 30 min at 35° to a mixture of ionic liquid (preparation from AlCl3 and 1-butyl-3-methylimidazolium chloride given) and o-xylene and the whole was stirred for 60 min at 35°, 60 min at 60° and 10 h at 120° to give reaction products comprising 2 liquid phases. The lower phase containing the ionic liquid was separated and returned to the precondensate rearrangement reaction step and the upper phase was worked up to give title polyamines in 35-45% yields.

ACCESSION NUMBER: 2002:941574 CAPLUS
DOCUMENT NUMBER: 138:25096
TITLE: Manufacture of polyamines of diphenylmethane series in presence of ionic liquids
INVENTOR(S): Koch, Daniel; Schelhaas, Michael; Grotjohann, Dirk
PATENT ASSIGNEE(S): Bayer AG, Germany
SOURCE: Ger. Offen., 6 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10127273	A1	20021212	DE 2001-10127273	20010605
PRIORITY APPLN. INFO.:			DE 2001-10127273	20010605

L14 ANSWER 2 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

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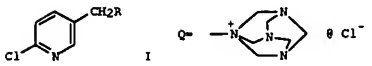

I

AB The title compds. (I; R = N:CH2), useful as an intermediate for drugs and agrochems., in particular insecticides, are prepared by (1) reaction of 2-chloro-5-trichloromethylpyridine, **hexamethylenetetramine**, and H in the presence of a hydrogenation catalyst or (2) hydrolysis of 2-chloro-5-pyridylmethylhexamethylenetetraammonium chloride I (R = Q) with H2O. I (R = N:CH2) is hydrolyzed to 2-chloro-5-aminomethylpyridine I (R = NH2) in the presence of a lower alc. while the byproduct **formaldehyde** is converted into di(lower alkoxy)methane and removed outside the reaction system. Thus, 2-chloro-5-trichloromethylpyridine 46.2, **hexamethylenetetramine** 56.0, Et3N 60.6, Raney nickel 4.6, H2O 84.5, and PhMe 46.2 g were added to an autoclave and stirred at 45° for 5 h while introducing H at 3 + 105 Pa to give 65.4% I (R = N:CH2) and 12.0% I (R = Q) vs. 4.2% I (R = N:CH2) and 79% I (R = Q) when the reaction was carried out in the absence of Et3N. The byproduct I (R = Q) 9.1, 28% aqueous NH3 1.83, H2O 11.5, and PhMe 6.9 g were added to a reactor and heated at 60° for 2 h to give 99.4% I (R = N:CH2) and 0.6% unreacted I (R = Q). I (R = N:CH2) (7.7 g) was suspended in 11.5 g PhMe, and to the suspension was added dropwise 15.6 g 36% concentrated aqueous HCl at 30° over 10 min and then added 12.8 g MeOH and the reaction mixture was stirred at 66° for 1 h and further reacted while **distilling** off MeOH and dimethoxymethane under normal pressure until the reaction temperature reached 100° and then neutralized with aqueous NaOH and extracted CHCl3 to give 96% I (R = NH2).

ACCESSION NUMBER: 1997:53901 CAPLUS
DOCUMENT NUMBER: 126:74753
TITLE: Method for producing **N-methylidene -2-chloro-5-pyridinemethaneamine**
INVENTOR(S): Aketada, Hiroyuki; Hitomi, Susumu; Matsunaga, Tomoko; Nagaoka, Masayo
PATENT ASSIGNEE(S): Koei Chemical Co, Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 08295670	A2	19961112	JP 1995-181738	19950718
PRIORITY APPLN. INFO.:			JP 1995-39825 A	19950228
OTHER SOURCE(S):	CASREACT 126:74753			

L14 ANSWER 3 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

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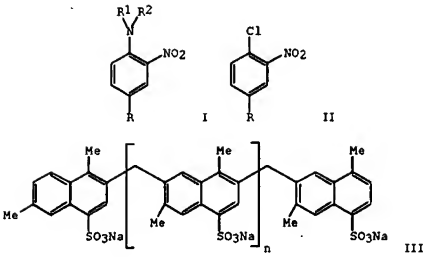

I II III

AB Nitroanilines I (R = H, NO2; R1, R2 = H, C1-4 alkyl) are prepared by aminolysis/ammonolysis of nitrochlorobenzenes II with 2000-4000 mol% HNR1R2 at 40-120° under atmospheric or elevated pressure in the presence of 0.1-10 weight% (vs. II) of an ionic or nonionic surfactant. For example, 1.83 mol 2-O2NC6H4Cl was added over 4 h to 4.02 mol HNMe2 (as 40% solution) and 10 g dimethylnaphthalenesulfonate-**formaldehyde** condensate III (n undefined) at 55-60°, followed by stirring 8 h at 60-70°, workup, and vacuum **distillation**, to give 93.2% 2-O2NC6H4NMe2 of 98.8% purity. Three addnl. examples are described, with 94.5-99.1% yields.

ACCESSION NUMBER: 1991:428869 CAPLUS
DOCUMENT NUMBER: 115:28869
TITLE: Preparation of nitroanilines by ammonolysis or aminolysis of nitrochlorobenzenes in the presence of surfactants
INVENTOR(S): Papenfuhs, Theodor; Hess, Reiner; Deubel, Reinhold; Jung, Ruediger
PATENT ASSIGNEE(S): Hoechst A.-G., Germany
SOURCE: Ger., 6 pp.
CODEN: GWXXAW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 3924092	C1	19901129	DE 1989-3924092	19890720
CA 2063817	AA	19910121	CA 1990-2063817	19900719
WO 9101292	A1	19910207	WO 1990-EP1180	19900719
W: CA, JP, US				
RW: AT, BE, CH, DE, DK, ES, FR, GB, IT, LU, NL, SE				
EP 483241	A1	19920506	EP 1990-911416	19900719

L14 ANSWER 3 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

R: BE, CH, DE, FR, GB, IT, LI, NL, SE				
JP 04506805	T2	19921126	JP 1990-510846	19900719
PRIORITY APPLN. INFO.:			DE 1989-3924092 A	19890720
			WO 1990-EP1180 W	19900719
OTHER SOURCE(S):	MARPAT 115:28869			

L14 ANSWER 4 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

AB The title compns., with low evolution of HCHO, contain N-methylol derivs. of amides, urethanes, ureas, or aminotriazines, or their ethers, and BF3, BF3 complexes, HBF4, or its salts. Stirring 70% aqueous 4,5-dihydroxy-N,N'-bis(hydroxymethyl)ethylene urea 2000, MeOH 580, and 51% methanolic BF3.MeOH 25 g at pH 1.6 and 40° for 4 h, cooling, adding 38.2 g 25% NaOH, and distilling MeOH at 40°/60-80 mm gave a 75% aqueous finish with pH 5.7. Cotton poplin (basis weight 140 g/m2) was treated (uptake 70%) with this solution containing 10 g/L MgCl2.6H2O and dried at 110° to 8% residual H2O to give a fabric with dry wrinkle recovery (DIN 53 890) 233, tenacity 270 N, and residual HCHO (AATCC 112) 154 ppm; vs. 254, 276, and 695, resp., when MeOH was omitted, and 110, 406, and 7, resp., to unfinished poplin.

ACCESSION NUMBER: 1991:410792 CAPLUS
DOCUMENT NUMBER: 115:10792
TITLE: Process for the production of aqueous solutions suitable for finishing cellulose-containing textile materials
INVENTOR(S): Bereck, Attila; Flory, Klaus; Kummer, Matthias
PATENT ASSIGNEE(S): BASF A.-G., Germany
SOURCE: Eur. Pat. Appl., 9 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 392349	A1	19901017	EP 1990-106514	19900405
EP 392349	B1	19940112		
R: AT, BE, CH, DE, DK, ES, FR, GB, IT, LI, NL, SE				
DE 3912084	A1	19901025	DE 1989-3912084	19890413
CA 2013060	AA	19901013	CA 1990-2013060	19900326
AT 100122	E	19940115	AT 1990-106514	19900405
ES 2047740	T3	19940301	ES 1990-106514	19900405
US 6001132	A	19991214	US 1990-504881	19900405
JP 02292249	A2	19901203	JP 1990-92362	19900409
JP 3130911	B2	20010131		

PRIORITY APPLN. INFO.: DE 1989-3912084 A 19890413
EP 1990-106514 A 19900405
OTHER SOURCE(S): MARPAT 115:10792

L14 ANSWER 5 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

AB Simple tests were evaluated for use in determining the condition and lifetime of industrial solvents such as cold dipping solvents (Stoddard solvent), vapor degreasing solvents (chlorinated hydrocarbons), and metal preparation or precision cleaning solvents (Freon 113 and isopropanol). The use of these tests to monitor the quality of reclaimed solvents was also explored. Visible absorption spectrometry was the most reliably measured property, followed by sp. gr., viscosity, and elec. conductivity To determine the concns. of antioxidants, acid acceptors, and metal stabilizers in chlorinated solvents, gas chromatog.-mass spectrometry was used. Reclamation studies on spent chlorinated solvents were carried out by using distillation and a carbon adsorption method.

ACCESSION NUMBER: 1990:534614 CAPLUS
DOCUMENT NUMBER: 113:134614
TITLE: Methods for monitoring solvent condition and maximizing its utilization
AUTHOR(S): Joshi, Surendra B.; Donahue, Bernard A.; Tarrer, Arthur R.; Guin, James A.; Rahman, Mahmud A.; Brady, Bill L., Jr.
CORPORATE SOURCE: U S Air Force (HQ AFESC/RDVS), Tyndall Air Force Base, Panama City, FL, 32403-6001, USA
SOURCE: ASTM Special Technical Publication (1989), 1043(Hazard. Ind. Solid Waste Minimization Pract.), 80-103
CODEN: ASTTA8; ISSN: 0066-0558
DOCUMENT TYPE: Journal
LANGUAGE: English

L14 ANSWER 6 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

AB The title polyamines are prepared with decreased energy consumption in distillation by polymerization of PhNH2 with HCHO followed by a series of extraction stages. A schematic diagram of the process is given. The 2-stage polymerization of PhNH2 with HCHO in the presence of HCl followed by continuous countercurrent extraction with a PhNH2-xylene mixture, a 2nd extraction, washing, and distillation, gave a mixture of 4,4'-methylenedianiline 46.3, 2,2'- and 2,4'-isomers 4.5, N-Me derivs. 0.2, triamines 22.2, tetramines 11.1, and polyamines with higher d.p. 15.6%.

ACCESSION NUMBER: 1989:633936 CAPLUS
DOCUMENT NUMBER: 111:233936
TITLE: Preparation of polynuclear aromatic polyamines
INVENTOR(S): Knoefel, Hartmut; Brockelt, Michael; Petinaux, Marcel; Uchdorf, Rudolf
PATENT ASSIGNEE(S): Bayer A.-G., Fed. Rep. Ger.
SOURCE: Eur. Pat. Appl., 14 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 337205	A2	19891018	EP 1989-105652	19890330
EP 337205	A3	19901212		
EP 337205	B1	19930113		
R: BE, DE, ES, FR, GB, IT, NL				
DE 3812083	A1	19891026	DE 1988-3812083	19880412
CA 1318076	A1	19930518	CA 1989-595201	19890330
ES 2053848	T3	19940801	ES 1989-105652	19890330
US 4924028	A	19900508	US 1989-335062	19890406
BR 8901716	A	19891121	BR 1989-1716	19890411
JP 02124855	A2	19900514	JP 1989-89891	19890411

PRIORITY APPLN. INFO.: DE 1988-3812083 A 19880412

L14 ANSWER 7 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN

AB N-Glycidylamines with high purity, low viscosity and improved storing properties are prepared by 2-stage addition of amines to epichlorohydrin (I) first at 65° to 60% conversion of functional groups and second at 66-120° followed by dehydrochlorination of the chlorohydrins with an alkali hydroxide. Thus, a mixture of 279.3 g aniline, 624 g 97.8% I, 300 g iso-BuCOMe, and 27 g water was heated to 60°, kept for 3 h, then at 85° for 5 h, cooled to 50°, treated with 750 g 40% NaOH for 4 h and finally heated 2 h at 80°. Treating the reaction mixture with 650 g water, then with 300 g iso-BuCOMe, washing the mixture 3 times with 225 g 5% salt, and distilling off iso-BuCOMe gave 590 g N,N-diglycidylaniline with 8.69 epoxy group equivalent/kg, 0.48% Cl, and viscosity 110 mPa-s/25°.

ACCESSION NUMBER: 1989:555027 CAPLUS
DOCUMENT NUMBER: 111:155027
TITLE: Preparation of aromatic N-glycidylamines
INVENTOR(S): Dobas, Ivan; Lunak, Stanislav; Makovsky, Leopold; Podzimek, Stepan; Macku, Vladislav; Rada, Antonin; Machovsky, Stanislav
PATENT ASSIGNEE(S): Czech.
SOURCE: Czech., 12 pp.
CODEN: CZXXA9
DOCUMENT TYPE: Patent
LANGUAGE: Czech
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 256646	B1	19880415	CS 1986-3580	19860516

PRIORITY APPLN. INFO.: CS 1986-3580 19860516
OTHER SOURCE(S): MARPAT 111:155027

L14 ANSWER 8 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB Ge adsorbent resins were prepared by polymerization of triethylenetetramine with epichlorohydrin followed by N-methylation with HCHO. The adsorption of Ge4+ onto the resins at different pH and in the presence of other metal ions (Ni2+, Zn2+, Fe2+) was studied. The resins were regenerated by washing with HCl followed by distilled water.

ACCESSION NUMBER: 1989:174267 CAPLUS
DOCUMENT NUMBER: 110:174267
TITLE: Synthesis and adsorption of germanium adsorption resin
AUTHOR(S): Fei, Wen; Liang, Liang
CORPORATE SOURCE: Hunan Univ., Changsha, Peop. Rep. China
SOURCE: Lizi Jiaohuan Yu Xifu (1988), 4(3), 190-3
CODEN: LJYXE5; ISSN: 1001-5493
DOCUMENT TYPE: Journal
LANGUAGE: Chinese

L14 ANSWER 9 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB The title compds. H2C:CR1CONHCH2OR2 (R1 = H, Me; R2 = Bu, CH2CHMe2, CHMeEt, CMe3), useful as crosslinking monomers for coatings, are manufactured by hydroxymethylating H2C:CR1CONH2 with HCHO in R2OH in the presence of an alkaline catalyst, etherifying the resulting H2C:CR1CONHCH2OH with addnl. R2OH in the presence of an acid catalyst, and distilling off the solvent at pH 2-5. Thus, 71.7 g acrylamide was treated with 56.3 g paraformaldehyde in 37.1 g BuOH at pH 10.0 (by Et3N) at 50° to give N-methylolacrylamide (I), which was treated with addnl. 425.2 g BuOH under reflux at pH 3.0 (by oxalic acid). The reaction mixture was readjusted at pH 3.0 by oxalic acid and concentrated under reduced pressure at 90° to give 163.2 g product containing N-butoxymethylacrylamide 98.2, I 0.3, and acrylamide 1.5%.

ACCESSION NUMBER: 1988:205254 CAPLUS
DOCUMENT NUMBER: 108:205254
TITLE: Method of making N-alkoxymethyl(meth)acrylamides
INVENTOR(S): Watanabe, Seiichi; Sakasai, Kazuya; Tanaka, Yoshinori
PATENT ASSIGNEE(S): Mitsui Toatsu Chemicals, Inc., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 5
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63005068	A2	19880111	JP 1986-146828	19860625
JP 07033362	B4	19950412		
PRIORITY APPLN. INFO.:			JP 1986-146828	19860625

OTHER SOURCE(S): CASREACT 108:205254; MARPAT 108:205254

L14 ANSWER 10 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB An ester (mono/di) of sucrose and p-[(HOCH2)2NCO]C6H4CO2H (I), sucrose etherified with (HOCH2)2NCOCH2CH2 and HOCH2NHCOCH2CH2 groups, a diester of sucrose and H2NCO(CH2)4CO2H, or a similar carbohydrate derivative is polymerized with HCHO and urea or melamine to prepare crosslinked resins with good elasticity and processability. Thus, 90 parts urea in 125 parts 37% HCHO solution was heated to 60°, adjusted to pH 8-9 with Na2CO3, heated for 45 min, mixed with an ester (mono/di) of sucrose and I 10, NH4Cl 1, and cellulose fibers or powder 30 parts, freed of solvent by distillation, dried at <50° in vacuo, and heated at 80° to prepare a molding composition which gave moldings with elastic modulus 49,583 daN/cm2.

ACCESSION NUMBER: 1981:16573 CAPLUS
DOCUMENT NUMBER: 94:16573
TITLE: Crosslinked resins from N-methylol group-containing carbohydrate derivatives
INVENTOR(S): Greber, Gerhard; Andres, Hans; Pichler, Werner
PATENT ASSIGNEE(S): Evidenzbuero Oesterreichischer Zuckerfabriken G.m.b.H., Austria
SOURCE: Austrian, 8 pp.
CODEN: AUXXAK
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
AT 359287	B	19801027	AT 1979-2747	19790412
AT 7902747	A	19800315		
DE 2928003	A1	19801023	DE 1979-2928003	19790711
PRIORITY APPLN. INFO.:			AT 1979-2747 A	19790412

L14 ANSWER 11 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB Carpets from polyacrylonitrile (I) [25014-41-9] and polypropylene [9003-07-0] fibers were made flameproof by treatment with a mixture of a phosphate, e.g. tris(2,3-dibromopropyl) phosphate (II) [126-72-7] and the reaction product of a methylolmelamine derivative, e.g. hexamethylolmelamine pentamethyl ether (III) [13822-63-4] and a phosphonopropionamide, e.g. N-methylol-3-(dimethylphosphono)propionamide (IV) [20120-33-6]. Thus, 211 parts IV and 71 parts 90% III were heated 50 min at 118-25.deg. (the last 30 min in vacuo), MeOH distilled, and 220 parts II added at 100.deg. to give a clear, viscous product. A I carpet (1500 g/m2) was padded with a 45% solution of the above product (100% impregnation), dried at 90.deg., heated 5 min at 155.deg., washed (for improvement of hand) in a bath containing 5 g Na2CO3/l. and 2 g 1:5 mole p-tert-C9H19C6H4O-ethylene oxide adduct 20 min at 40.deg., and dried at 90.deg. to give a flameproof (DIN 51 960) carpet.

ACCESSION NUMBER: 1972:60868 CAPLUS
DOCUMENT NUMBER: 76:60868
TITLE: Flameproofing of carpets
INVENTOR(S): Mayer, Fritz; Nachbur, Hermann; Kern, Joerg; Maeder, Arthur
PATENT ASSIGNEE(S): Ciba-Geigy A.-G.
SOURCE: Ger. Offen., 40 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2109702	A	19710930	DE 1971-2109702	19710302
CH 703541	A4	19720131	CH 1970-354170	19700310
CH 523373	A	19720531	CH 1970-523373	19700310
IL 36308	A1	19740516	IL 1971-36308	19710301
ZA 7101385	A	19720223	ZA 1971-1385	19710303
NO 129008	B	19740211	NO 1971-810	19710303
FR 2081816	A5	19711210	FR 1971-7974	19710308
FR 2081816	B1	19740215		
PL 83046	P	19751231	PL 1971-146733	19710308
BE 763974	A1	19710909	BE 1971-100659	19710309
NL 7103132	A	19710914	NL 1971-3132	19710309
AT 319181	B	19741210	AT 1971-2023	19710309
GB 1331346	A	19730926	GB 1971-23110	19710419
PRIORITY APPLN. INFO.:			CH 1970-3541 A	19700310

L14 ANSWER 12 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB 1,3-Propanolamine was mixed at 40° with aqueous HCHO, and the solution was continuously fed into a tubular reactor, containing a catalyst with 17.5% Co, 0.9% Cr and 0.36% P2O5 on SiO2, at 300 atm H pressure and 140°. The mixture was distilled to give 90 weight % N,N-dimethyl-1,3-aminopropanol. Similarly prepared were PhCH2NHMe, N-methylmorpholine, tetramethylethylenediamine , N,N-dimethyl-1,3-propylenediamine, N-methylcyclohexylamine and N-methylpiperidine.

ACCESSION NUMBER: 1971:124791 CAPLUS
DOCUMENT NUMBER: 74:124791
TITLE: Secondary and tertiary amines
PATENT ASSIGNEE(S): Badische Anilin- & Soda-Fabrik AG
SOURCE: Fr. Demande, 8 pp.
CODEN: FRXXBL
DOCUMENT TYPE: Patent
LANGUAGE: French
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 2017634		19700522	FR	
DE 1793380			DE	
GB 1276740			GB	
PRIORITY APPLN. INFO.:			DE	19680909

L14 ANSWER 13 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB Hard, elastic coatings and films are prepared by mixed polycondensation of polyesters of mol. weight 600-3000 with aminoplast resins. Thus, a polyester (I) of acid number 12.2 mg KOH/g is prepared by polycondensation of 1,4-bis(hydroxymethyl)cyclohexane (II) and ethylene glycol with phthalic anhydride (III) and adipic acid (IV) and modification with maleic anhydride (V). Melamine, paraformaldehyde, BuOH, and HCO2H are refluxed to obtain a clear solution, which is treated with a 60% xylene solution of I and the reaction mixture distilled to yield a coating composition, which is pigmented with TiO2 and sprayed onto metals to yield a hard elastic coating. Other polyesters used are prepared by condensing II and 1,2-propanediol with III and IV and modifying with V or III. Other aminoplast resins used are prepared by condensing urea with HCHO and BuOH or iso-PrOH.

ACCESSION NUMBER: 1971:14269 CAPLUS
DOCUMENT NUMBER: 74:14269
TITLE: Coating compositions containing a hydroxyl and carboxyl polyester and a N-methylol polymer
INVENTOR(S): Schuetze, Ernst C.; Riemhofer, Franz; Dittmann, Walter
PATENT ASSIGNEE(S): Chemische Werke Huels A.-G.
SOURCE: Ger. Offen., 16 pp. Addn. to Ger. Offen. 1644769
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1900414	A	19700924	DE 1969-1900414	19690104
DE 1900414	B2	19770505		
DE 1900414	C3	19771229		
JP 49020611	B4	19740525	JP 1969-54204	19690710
PRIORITY APPLN. INFO.:			DE 1968-1811632 A	19681129
			DE 1969-1900414 A	19690104

L14 ANSWER 14 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB Polyepoxides are cured with a reaction product of a dihydroxydiphenyl sulfone, an amine, and an aldehyde. Thus, 1000 g. 37% aqueous solution of HCHO was added during 60 min. to 2222 g. of an aqueous solution of Me2NH at <30°. After addition of HCHO, the mixture was stirred 2 hrs. at 25-30°. To 1044 g. of this mixture, was added 250 g. 4,4'-dihydroxydiphenyl sulfone. This mixture was slowly heated to reflux under atmospheric pressure and refluxed for 2 hrs. The contents were then distilled at 50 mm. to a pot temperature of 120°. The residue, 447 g., was wine-colored, and cooled to a brittle solid at .apprx.25°. Similarly prepared were curing agents from N-methylethanolamine and bis(3-aminopropyl) ether of diethylene glycol and from 3,3'-dimethyl-4,4'-dihydroxydiphenyl sulfone. The curing agents produced by this method are used in the conventional manner.

ACCESSION NUMBER: 1967:19200 CAPLUS
DOCUMENT NUMBER: 66:19200
TITLE: Polyepoxide curing agents
INVENTOR(S): Sellers, Ralph F.
PATENT ASSIGNEE(S): Union Carbide Corp.
SOURCE: U.S., 8 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3285991		19661115	US	19630326

L14 ANSWER 15 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB The title compds. I and the intermediates II and salts thereof are prepared by standard methods and are useful as tranquilizers, psychic stimulants, diuretics, antihistamines, and inhibitors of pseudocholinesterase and O-methyltransferase. Salts with H2SiF6 are useful as moth-killing agents and derivs. with thiocyanate-formaldehyde consdensation products as pickling inhibitors. Thus, to a mixture of 600 g. 1-bromo-2-nitrobenzene, 300 g. anthranilic acid, and 300 ml. n-amyl alc. was added with stirring at 80-90° 3.0 g. Cu powder and 300 g. K2CO3. The temperature rose to 120° and the mixture was heated 3 hrs. at 200-10° and worked up to yield 92% N-(2-nitrophenyl)anthranilic acid (III), m. 219° (AcOH). A mixture of 348 g. III in 10 l. dry MeOH was treated with stirring 7 hrs. on a steam bath with gaseous HCl to yield 86% methyl N-(2-nitrophenyl)anthranilate (IV), m. 156-7° (MeOH). A solution of 299.2 g. IV in 8 l. absolute MeOH was hydrogenated 24 hrs. with 100 ml. Raney Ni suspension and 3.5 atmospheric H at 25° to yield 85% methyl N-(2-aminophenyl)anthranilate (V), m. 102-3° (EtOH-H2O). V (169.4 g.) was heated 1 hr. in an oil bath at 240-50° and worked up to yield 86% 5H-dibenzo[b,e] [1,4]diazepin-11(10H)-one (VI), m. 254-5° (C5H5N). To a solution of 139.0 g. 3-bromopropanol in 200 ml. absolute MeOH was added dropwise in 10 min. with stirring under N a solution of 121.2 g. N-benzyl-methylamine in 50 ml. absolute MeOH. After 20 min., the solution started refluxing for 1 hr. and was then heated 16 hrs. with stirring under reflux, to yield 151.7 g. (from 2 reactions) 3-(N-benzylmethylamino)propanol (VII), b0.15-0.17 94-7° n25D 1.5203. To a solution of 150 g. VII in 200 ml. dry C6H6 was added dropwise with stirring under N in 1 hr. a solution of 200 g. SOCl2 in 100 ml. dry C6H6. The mixture was refluxed 8 hrs. to yield after 3 days at 25° 120.6 g. 3-(N-benzylmethylamino)propylchloride (VIII), b0.60 104.5-6° n25D 1.5150; VIII.HCl m. 86-93°. Similarly were prepared 3-dibenzylaminopropanol, 3-dibenzylaminopropyl chloride and its HCl salt. To a solution of 31.5 g. VI in 450 ml. dioxane (distilled from LiAlH4) was added with stirring 6.0 g. NaNH2 in small portions in 1 hr., and the mixture was refluxed 3.5 hrs. To this mixture was added dropwise at 70° in 30 min. 20.4 g. freshly distilled 2-diethylaminoethyl chloride and the mixture was refluxed 4 hrs. to yield 67% 10-(2-diethylaminoethyl)-5H-dibenzo[b,e][1,4]diazepin-11(10H)-one (IX), m. 132-3° (iso-PrOH). Similarly were prepared the following 10-substituted 5H-dibenzo[b,e][1,4] diazepin-11(10H)-ones (substituent, yield, and m.p. given): 3-dimethylaminopropyl (X), 50%, 119-21°; 3-N-benzylmethylaminopropyl (XI), --, -- (from VI, VIII, and NaH in DMF); 3-diethylaminopropyl (XII), --, 77-8°. A solution of 40.0 g. XI in 400 ml. absolute MeOH was hydrogenolyzed 16 hrs. at 3.8 atmospheric over 4.0 g. 10% Pd-C to yield 10-(3-methyl-aminopropyl)-5H-dibenzo[b,e][1,4] diazepin-11(10H)-one (XIII).-HCl, hygroscopic solid. To a mixture of 6.1 g. IX in 250 ml. dry Et2O was added with stirring under N 1.1 g. LiAlH4; the mixture was refluxed 30 hrs. to yield 71% 10-(2-diethylaminoethyl)-10,11-dihydro-5H-dibenzo[b,e][1,4]diazepine-2HCl, m. 199.5-200.5° (decomposition). Similarly were prepared the following 10-substituted 10,11-dihydro-5H-dibenzo[b,e][1,4]diazepines (starting compound, substituent, yield salt, and m.p. given): X, 3-dimethylaminopropyl, --, di-HCl, 176-7°; XIII, 3-methylaminopropyl, --, di-HCl, hygroscopic solid (iso-PrOH-Et2O); VI, H, 60%, --, 196.5-201° (iso-PrOH); XII, 3-diethylaminopropyl, --, di-HCl, --. Starting with the appropriate substituted aminoalkyl chlorides were prepared the following 10-substituted 5H-dibenzo-[b,e][1,4]diazepin-11(10H)-ones (substituent given, and the

L14 ANSWER 15 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
corresponding 10-substituted 10,11-dihydro-5H-dibenzo[b,e][1,4] diazepines (and HCl salts, no phys. consts. given): 3-dibenzylaminopropyl (XIV) (no dihydro deriv. prepd.); 2-(dibutylamino)-ethyl; 2-diisopropylaminoethyl; 2-dimethylaminoethyl; 4-dimethylaminobutyl; 2-(1-pyrrolidyl)ethyl; 2-(2,2-dimethyl-1-pyrrolidyl)ethyl; 3-(4-methyl-1-piperazinyl)propyl; 2-(1-piperidyl)ethyl; 2-(4-propyl-1-piperidyl)ethyl; 2-hexamethylenimino)ethyl; 2-(2-methylhexamethylenimino)ethyl; 2-(4-morpholinyl)ethyl; 2-(2-methyl-4-morpholinyl)ethyl; 2-(4-thiamorpholinyl)ethyl; 3-aminopropyl (from XIV, using the method for XIII). Also were prepd. the following substituted III (substituent given, no phys. consts.): 5-Cl; 4-Cl; 3-Me; 4-tert-Bu; 6-F; 4,5-Me2; 3-MeO-4-Me; 4-EtO. The following N-(2-nitro-substituted phenyl)anthranilic acids were also prepd. (substituent given): 4-tert-Bu; 3-Et; 4,5-F2; 4,5(BuO)2; 4,5,6-(MeO)3; 5-CF3. Prepd. were N-(4-chloro-2-nitrophenyl)-5-chloroanthranilic acid and N-(4-methoxy-2-nitrophenyl)-5-methoxyanthranilic acid; the corresponding Me, Et, Pr, and Bu esters of these anthranilic acids; the corresponding amino esters. Also prepd. were the following substituted VI: 4-Me; 3-Cl; 3-tert-Bu; 7,8-F2; 8-tert-Bu; 6,7,8-(MeO)3; 7-CF3; 9-Et; 2-Cl; 1-F; 2,3-Me2; 4-MeO-3-Me; 3-EtO; 2,8-Cl2; 2,8-(MeO)2; 7,8-(BuO)2. Also prepd. were the corresponding 10,11-dihydro substituted 5H-dibenzo[b,e] [1,4]diazepines. The substituted VI were converted with 3-dimethylaminopropyl chloride into the corresponding 10-(3-dimethylaminopropyl)-substituted 5H-dibenzo[b,e][1,4]diazepin-11(10H)-ones, and reduced to yield the corresponding 10,11-dihydro-10-(3-dimethylaminopropyl)-substituted 5H-dibenzo[b,e][1,4]diazepines and di-HCl salts. Cf. CA 63, 2859h and 14641g.

ACCESSION NUMBER: 1966:43917 CAPLUS
DOCUMENT NUMBER: 64:43917
ORIGINAL REFERENCE NO.: 64:8218g-h,8219a-h
TITLE: Substituted 10,11-dihydro-5H-dibenzo [b,e] [1,4] diazepines
PATENT ASSIGNEE(S): Upjohn Co.
SOURCE: 40 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 297030		19650525	NL	
PRIORITY APPLN. INFO.:			US	19620828

L14 ANSWER 16 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB Amines with the general formula I, where n is 0-3, R1, R2, and R3 are H or Me, R4 is an alkyl group, and R5 is H or an alkyl group, can be prepared from an aminophenol with the general formula II, where R4' is H or an alkyl group, and R5' is H, acyl, or an alkyl group, and alcohols of the general formulas CH2:CHC(CH3)(OH)[CH2CH2CH2CH(CH3)]CH3 or HOCH2CH:C(CH3)nCH2CH2CH2CH(CH3)nCH3 or their esters. Thus, to a mixture of 11. freshly distilled formic acid (99%) and 120 g. 2,3,5-trimethyl-4-formylaminophenol, 200 g. isophytol was added. With addition of N2 and refluxing, mixture was stirred for 22 hrs. at 135°. After cooling mixture was poured on 2 kg. ice and a brown oil formed. Yield was 130 g. α- tocopheramine, b0.01 200-3°, absorption maximum at 300 mμ (E11 85), which was acylated and then reduced to give N-ethyl-γ- tocopheramine, a light yellow oil, b0.01 211-14°, uv absorption maximum at 299 mμ (E11 52), n24.5D 1.5096. Similarly obtained, starting with 2,3-dimethyl-4-formylaminophenol, was N-ethyl-γ- tocopheramine, b0.05 195-7°, uv absorption maximum at 238 and 305 mμ (E11 195 and 69), n22.5D 1.5083. In 9 g. dry formic acid, 10 g. α-tocopheramine and 6 g. of a 40% formaldehyde solution were heated for 16 hrs. to boiling. Yield was N,N-dimethyl-γ-tocopheramine, b0.02, 200-5°, n23D 1.5015. Similarly obtained, starting with δ- tocopheramine, was N,N-dimethyl-δ- tocopheramine, b0.007 183-8°, n19D 1.5080, absorption maximum at 244 and 304 mμ (E11 268 and 58). In 1 l. dry formic acid 174 g. N-formyl-2,3-dimethyl-4-aminophenol was dissolved under N2, 220 g. isophytol was added, and the mixture refluxed for 22 hrs. after which it was poured on 2 kg. ice. Yield was N-formyl-γ tocopheramine, b0.01 233°, n24.5D 1.5158, which was reduced to yield N-methyl-γ- tocopheramine, a light yellow oil, b. 190-5°, n22D 1.5083, absorption maximum at 306 mμ (E11 74). Similarly obtained, starting with N-formyl-δ-tocopheramine, was N-methyl-δ-tocopheramine, b0.005 189-90°, n22.5D 1.5106, uv absorption maximum at 242 and 309 mμ (E11 225 and 66). Also obtained starting with N-formyl-β- tocopheramine, was N-methyl-β- tocopheramine, b0.03 207-10°, n21D 1.5088, absorption maximum at 234 and 300 mμ (E11 182 and 77). The compds. are useful as anti-oxidants.

ACCESSION NUMBER: 1966:4088 CAPLUS
DOCUMENT NUMBER: 64:4088
ORIGINAL REFERENCE NO.: 64:707e-h,708a
TITLE: Amines
PATENT ASSIGNEE(S): F. Hoffmann-La Roche & Co., A.-G.
SOURCE: 9 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 6414649		19650621	NL	
PRIORITY APPLN. INFO.:			CH	19631220

L14 ANSWER 17 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB 3-Aminoalkyl-substituted indazoles (I) which, by analogy with tryptamine and hydroxytryptamine, might be expected to have similar biol. activity, were prepared The simple analogs (R = H or OH, R1 = CH2CH2NH2) were prepared by Ainsworth (CA 52, 3785b, 11011f) from the corresponding indazole-3-carboxylic acid derivs. The present authors sought to prepare such compds. by applying a Mannich reaction with formaldehyde and ammonia or an amine to 3-methylindazole I (R = H, R1 = Me), but without success. Nor could they induce 3-benzylindazole, which they prepared in two ways from o-bromophenyl benzyl ketone and N-nitroso-o-acetamidodibenzyl, resp., to undergo this reaction. They sought therefore to obtain from o-nitroacetophenone the Mannich bases, β-dimethylaminoethyl (IIa), β-piperidylethyl (IIb), and β-(N-methylcyclohexylamino)ethyl (IIc) O-nitrophenyl ketone with a view to converting them to 3-(β-dimethylaminoethyl), 3-(β-piperidylethyl),, or 3-[β-(N- methylcyclohexylamino)ethyl]indazoles by the Fischer method, viz., reduction of the NO2 group, diazotization, reduction to the hydrazine, and ring closure. The Mannich bases obtained in salt form, however, differed from those obtained in this way by Mannich and Dannehl (CA 32, 62336) and were identified, by empirical formula, spectrographic measurements, and reaction with ozone, as compds. formed by reaction of a second mol. of HCHO and having the structure III. Despite varying the conditions, they were not able to obtain IIa. Their own base IIIa resinified immediately on liberation from its salt. On subjecting its HCl salt to the above mentioned series of reactions (Fischer) without isolation of intermediates and at acid pH throughout, there were obtained the expected 3-(N-substituted-β-aminoisopropyl)indazoles corresponding to formula I, in which R is H and R1 is CHMeCH2NRR1, remembering that the methylene is reduced to Me. If the Mannich reaction is applied to the homologous o-nitropropiophenone, then the N-substituted-β-aminomethyl group should add on to the CH2 proximal to the CO and form a Mannich base corresponding to III, with the methylene reduced to Me. This on undergoing the same Fischer reactions as before should produce the same 3-(N-substituted-β-aminoisopropyl)indazoles. Although the authors obtained one of these by using Me2NH.HCl in the Mannich reaction, it proceeded with such difficulty and the overall yield was so small that its value as a structural proof was largely vitiated. These 3-β-aminopropylindazole products, unlike the usual Mannich bases, are stable. The benzoyl derivative of the dimethylamino product was prepared and it was also nitrated to the 5-nitro derivative, but the corresponding 5-amino derivative formed by hydrogenation proved to be unstable. A comparable nitration and reduction of 3-methylindazole as a model substance produced however the known 5-aminomethylindazole. The following are the more important exptl. data. o-Bromophenyl benzyl ketone (50.7 g.) heated 18 hrs. in a sealed tube with 80 ml. hydrazine hydrate at 200°, the product extracted into ether, washed with HOAc, KHCO3, and water, and evaporated and the residue distilled at 155°/0.01 mm. gave 14.5 g. 3-benzylindazole, prisms, m. 113-15° (ether/petr. ether). Also, 16.5 g. o-nitroacetophenone refluxed with 6 g. HCHO and 8.2 g. Me2NH.HCl in 40 ml. HOAc 3 hrs., and the distilled in vacuo gave 21.4 g. IIIa.HCl, m. 213-15° (decomposition). This (1.08g.) in 3 ml. HOAc, 10 ml. alc., and 2 ml. ZN HCl was hydrogenated in the presence of 0.2 g. 5% Pd-C at 26°/715 mm., and the residue crystallized from iso-PrOH-ether to give a product, m. 118-24°. This di-HCl salt (16.3 g.) in 50 ml. concentrated HCl diazotized with 4.2 g. NaNO2 in 40 ml. water, then added during 30 min. portionwise to 500 ml. saturated aqueous SO2

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while SO2 was passed in and, after standing, concd. in vacuo to 200 ml., boiled, and then evapd. to dryness in vacuo, treated with NH4OH, extd. into ether and then into dil. HOAc, and made alk. with NH4OH, and the pptd. bases shaken with ether gave 8.8 g. I (R = H, R1 = CHMeCH2NMe2), b0.01 122-3, recrystd. from petr. ether to give 5.5 g. prisms, m. 70-2°.

ACCESSION NUMBER: 1964:16678 CAPLUS
DOCUMENT NUMBER: 60:16678
ORIGINAL REFERENCE NO.: 60:2923e-h,2924a-d
TITLE: 3-(β-Aminopropyl)indazole derivatives
AUTHOR(S): Hunziker, F.; Lehner, H.; Schindler, O.; Schmutz, J.
SOURCE: Pharmaceutica Acta Helvetiae (1963), 38(7-8), 539-46
CODEN: PAHEAA; ISSN: 0031-6865
DOCUMENT TYPE: Journal
LANGUAGE: German

L14 ANSWER 18 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB The acid hydrolysis of arylamino acetals (I) leads to polymers formed by the crotonization of the corresponding amino aldehydes, but benzylamino acetals can be converted under the same conditions to characteristic derivs. of (PhCH2)2NCH2CHO formed by the hydrolysis of the corresponding acetal. A series of α-substituted I was prepared by the condensation of the appropriate halo acetal with suitable arylamines in the presence of NaNH2 or by the reaction of the appropriate arylimino acetals (II) with Grignard reagents. The II were prepared by the condensation of glyoxal hemiacetal with arylamines. The cyclization of the α-substituted I to substituted indoles takes place in the presence of BF3; a mechanism for this reaction is proposed. PhNH2 (20 g.) in 10 cc. dry Et2O and 5 g. powdered NaNH2 refluxed 1 hr. under a stream of N to remove the NH3 liberated, the mixture treated with 15.2 g. ClCH2CH(OEt)2(III) [or 21 g. BrCH2CH(OEt)2 (IV)] in 15 cc. dry Et2O, kept 1 hr. at room temperature, evaporated, the residue heated 0.5 hr. at 150°, cooled, diluted with Et2O, filtered off, and the crude product treated with 50% aqueous KOH and extracted with Et2O yielded 15.5 g. PhNHCH2CH(OEt)2 (V), b18 164°. Similarly was prepared the m-Me derivative of V, yellow liquid, 44%, b16 164-5°, n21D 1.5095. 3,4-(MeO)2C6H3 NO2 in EtOAc hydrogenated over Raney Ni in the presence of KOH yielded 85% 3,4-(MeO)2C6H3NH2 (VI). VI (15.3 g.) and 19.8 g. IV in 50 cc. EtOH refluxed 24 hrs. with 12.6 g. NaHCO3, concentrated, diluted with H2O, and extracted with Et2O gave 6.5 g. 3,4-di-MeO derivative of V, b1 140-2°, n21D 1.526, which turns black rapidly. Similarly were prepared PhMeNCH2CH-(OEt)2, b13 150-2°, n19D 1.514, 62%, and EtPhNCH2CH(OEt)2, yellowish liquid, b15 157-8°, n20D 1.509, 65%. V (15.6 g.) in dry Et2O added slowly to 10.2 g. Ac2O in 30 cc. dry Et2O, the mixture stirred 2 hrs., kept 24 hrs. at room temperature, and distilled yielded 90% AcPhNCH2CH(OEt)2, b13 171-3° (ligroine, b. 60-80°). HC(OEt)2 (160 cc.) and 70 cc. PrOH treated with a boiling solution of 3 g. NH4NO3 in 50 cc. absolute EtOH, and the mixture stirred overnight, filtered, and distilled gave 43 g. EtCH(OEt)2 (VII), b. 123-4°, n21D 1.383. CaCO3 (40 g.) and 100 g. VII treated dropwise with stirring at 8-10° with 126 g. Br (small amts. of Et2O were added occasionally), and the mixture filtered and worked up gave 107.2 g. MeCHBrCH(OEt)2 (VIII), b16 70-1°, n21D 1.4440. VII (132 g.) in 150 cc. CCl4 irradiated at 40° with a 60-w. bulb and treated with 178 g. N-bromosuccinimide in portions, and the mixt. filtered and distilled yielded 132.5 g. VIII, b13 66-7°. NaNH2 and 19 g. PhNH2 in 10 cc. dry Et2O refluxed 1 hr. under a stream of N, treated slowly with 21.1 g. VIII in 5 cc. dry Et2O, the whole refluxed 1 hr. and evaporated, and the residue heated 1 hr. at 150°, cooled, diluted with Et2O, and treated with 50% aqueous KOH gave from the Et2O phase 6.3 g. PhNHCHMeCH(OEt)2 (IX), b15 142-3°, n20D 1.5075. Similarly were prepared the following compds. (b.p./mm., nD/t°, and % yield given): o-Me derivative (X) of IX, 144-5°/13, -, 24; m-Me derivative (XI) of IX, 150°/14, 1.5080/20°, 24; p-Me derivative (XII) of IX, 153-5°/14, 1.5071/18°, 25. CH2:CHCHO (44 g.) and 144 g. HC(OEt)3 treated with 3 g. NH4NO3 in 50 cc. absolute EtOH, kept 8 hrs. at room temperature, and worked up yielded 76 g. CH2:CHCH(OEt)2 (XIIa), b. 123-5°, n21D 1.403. XIIa (65 g.) in 600 cc. H2O treated with 80 g. KMnO4, in 1600 cc. H2O at 5° at the rate of 25 cc./min., kept 2 hrs. at room temperature, heated 1 hr. on a water bath, cooled, centrifuged,

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satd. with K2CO3, and extd. with Et2O gave 30.9 g. HOCH2CH(OH)CH(OEt)2 (XIIb), b18 130-2°, n19D 1.4358; 6.5 g. 2nd crop. Pb(OAc)4 (177.2 g.) added to 65.6 g. XIIb in 800 cc. C6H6, treated after the exothermic reaction subsided with a few drops XIIb, stirred 2 hrs. at room temp., filtered, and distd. to 82° vapor temp., and the residue extd. with Et2O yielded 27.7 g. OHCCH(OEt)2 (XIII), b12-13 42-3°, n20D 1.399. PhNH2 (14.7 g.) in 100 cc. dry MePh treated with 21 g. XIII in 50 cc. dry MePh, refluxed 1 hr. with the azeotropic removal of H2O, and distd. gave 27.1 g. PhN:CHCH(OEt)2 (XIV), b15, 139-40°, n20D 1.5210, d. 1.035. Similarly were prepd. the following compds. (b.p./mm., nD/t°, d./t°, and % yield given): m-Me deriv. of XIV, 147-8°/13, 1.505/21°, 0.998/20°, 74; o-Me deriv. of XIV, 151-2°/14, 1.510/19°, 0.987/20°, 73; p-Me deriv. of XIV, 155-6°/16, 1.513/24°, 1.006/21°, 73. XIV (21 g.) in 30 cc. Et2O added dropwise at 0° with stirring to MeMgI from 21.4 g. MeI and 3.6 g. Mg, refluxed 1 hr., kept 15 hrs. at room temp., and worked up gave 15.2 g. IX, b13 143-4°, n22D 1.507, d23 0.988. IX refluxed 1 hr. with PhNCO in ligroine, b. 100-20°, gave the phenylurea deriv., m. 72-3° (ligroine). Similarly were prepd. the following compds. (% yield, b.p./mm. or m.p., nD/t°, d./t°, and m.p. of phenylurea deriv. given): α-Et analog (XV) of IX, 86, 148-9°/13, 1.506/20°, 0.987/18°, 102° (ligroine, b. 60-80°); α-Ph analog of IX, 70, 127-8°/1, 1.5495/25°, 1.045/ 20°, 112-13° (ligroine); X, 72, 149-50°/13, 1.503/22°,--, --; o-MeC6H4NHCHEtCH(OEt)2 (XVI), --, 149-50°/13, -, 1.500/20° 0.960/18°, -; α-Ph analog of XVI, 62, 53-4° (ligroine), --, --, --; XI, 72, 151-2°/13, 1.506/16°, 0.975/17°, 62° (ligroine); m-MeC6H4NHCHEtCH(OEt)2 (XVII), 71, 153-5°/14, 1.503/18°, 0.946/18°, --; α-Ph analog of XVII, 69, 140-1°/1, 1.547/20°, 1.036/21°, --; XII, 73, 155-6°/14, 1.505/22, 0.980/23, 82° (ligroine); p-isomer (XVIII) of XVII, -, 162-3°/15, 1.500/24°, 0.976/20°, 83° (ligroine); p-MeC6H4-NHCHPhCH(OEt)2, 69, 68° (ligroine), --, --, -- AcPh (60g.) and 250 cc. AcOH treated below 60° 4 hrs. with dry Cl, poured onto 1.5 l. crushed ice, and extd. with C6H6 yielded 7.9 g. BzCHCl2 (XIX), b15 135-6°. XIX (60 g.) in 150 cc. abs. EtOH added dropwise at 0° to NaOEt from 16 g. Na in 280 cc. abs. EtOH, kept 24 hrs. at room temp., filtered, concd., refiltered, dild. with 100 cc. H2O, and extd. with Et2O yielded 38.6 g. BzCH(OEt)2 (XX), b2 89-90°, n19D 1.494. XX (23.4 g.) in 50 cc. dry MePh added to 10.4 g. PhNH2 in 100 cc. dry MePh, refluxed 1 hr. with the azeotropic removal of H2O, and distd. gave 19.5 g. PhN:CPhCH(OEt)2 (XXI), viscous yellowish liquid, b1 135°, n21D 1.5550. XXI (5.7 g.) in 100 cc. abs. EtOH treated with 6 g. Na in portions, concd., poured into 50 cc. H2O, and extd. with Et2O gave 4.9 g. α-Ph analog of IX, b1 129-30°, n19D 1.5555. NaNH2 (5 g.), 5 cc. dry Et2O, and 42.8 g. MeNHPh in 20 cc. dry Et2O refluxed 2 hrs. under a stream of N, treated dropwise with 42.2 g. VIII in 10 cc. dry Et2O, refluxed 2 hrs., heated 4 hrs. at 130-5°, cooled, treated with 50 cc. 50% aq. KOH, and extd. with Et2O yielded 4.8 g. α-Me deriv. (XXII) of IX, b13 145-6°, n4D 1.514, d20 0.9885. III (40 g.) and 40 g. MeNH2 (or 123 g. 33% aq. MeNH2) heated 20 hrs. in an autoclave at 110°, cooled, treated with 100 cc. 50% aq. KOH, and extd. with Et2O yielded 23.8 g. MeNHCH(OEt)2 (XXIII), b16 60-1°, n20D 1.4190, and 2.4 g. MeN[CH2CH(OEt)2]2, b16 135-6°. III (16 g.) and 25 g. PhCH2NH2 heated 3 hrs. at 140-50°, cooled, filtered from 13.5 g. PhCH2NH2.HCl, and worked up gave 15.5 g. PhCH2NHCH2CH(OEt)2 (XXIV), b15 155-6°, n21D 1.4920.

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XXIII (14 g.) treated dropwise at 100° with 6.4 g. PhCH2Cl, heated 4 hrs. on a water bath, cooled, treated with 25 cc. 50% aq. KOH, and extd. with Et2O gave 10 g. PhCH2NMeCH2CH (OEt)2, b19 149-50°, n20D 1.4935. XXIV (44.7 g.) treated dropwise at 100° with 12.7 g. PhCH2Cl, heated 3 hrs. on a water bath, and worked up in the usual manner gave 24 g. (PhCH2)2NCH2-CH(OEt)2 (XXV), b0.02 118°, n20D 1.5235. (PhCH2)2NH (25 g.) and 7.6 g. III or 10 g. IV heated 6 hrs. at 130° yielded 5.9 g. XXV; the crude product from a similar run distd. at 15 mm. gave 5 g. (PhCH2)2NCH:CHOEt, b15 210-12°, n20D 1.5430. XXIV (4 g.) in 24 cc. concd. HCl heated 45 min. at 50°, cooled, and the resulting product dissolved in H2O, basified with NaOH, and extd. with Et2O gave an oily base which did not crystallize and could not be distd. XXV (3.2 g.) and 2.5 g. 10N HCl heated 70 min. on a steam bath, cooled, treated with 0.695 g. NH2OH.HCl in 2.5 cc. H2O and 3 g. KHCO3, heated 1.5 hrs. on a steam bath, cooled, and filtered gave (PhCH2)2NCH2CH:NOH, m. 82-3° (ligroine). XXV (1 g.) and 55 cc. 2N HCl heated 1 hr. on a steam bath and treated with 1 g. H2NCONHNH2.HCl and 1.5 g. NaOAc in H2O gave (PhCH2)2NCH2CH:NNHCONH2, m. 228° (50% EtOH). XXV (6.2 g.) added dropwise to 9.4 g. AcCl, heated 1 hr. on a water bath, and cooled gave 0.9 g. (PhCH2)2NH.HCl, m. 255-6° (sublimed). H2NCH2CH2OH (30.5 g.) treated dropwise at 40° with 63.5 g. PhCH2Cl below 100° heated 2.5 hrs. at 100-10°, treated with 20 g. NaOH in 30 cc. H2O, heated again 1 hr. at 100°, cooled, and extd. with C6H6 yielded 41.6 g. (PhCH2)2NCH2CH2OH (XXVI), b0.8 158-9°, m. 46-7°. (PhCH2)2NH (26 g.) heated on the water bath and treated dropwise with 8 g. ClCH2CH2OH, heated 2 hrs., basified, and extd. with C6H6 gave 11 g. XXVI, b2 170/170° (PhCH2)2NH (49.3 g.) in 75 cc. EtOH treated below 35° with stirring with 24 g. 37% aq. CH2O, 12.5 g. NaCN, and 21 cc. concd. HCl, kept 2 hrs. at room temp., refluxed 6 hrs., dild. with H2O, and extd. with CHCl3 yielded 50.5 g. (PhCH2)2NCH2CN (XXVII), b0.3 149-50°, m. 46-7°. XXVII (2.4 g.) in dry EtOAc (satd. at 0° with dry HCl) treated at 0° with 2.49 g. SnCl2 in 12 cc. EtOAc, kept 2 hrs. at 0°, refluxed 1 hr. with 10 cc. H2O, blow 1 with steam, cooled, and filtered gave (PhCH2)2NH.HCl, m. 256°. XXVII (7.2 g.)in 20 cc. dry Et2O refluxed 4 hrs. with 0.35 g. LiAlH4 and worked up gave (PhCH2)2NH. XXIV (11.2 g.), 13.8 g. o-C6H6(OMe)2, and 15 cc. AcOH treated dropwise at 0° with stirring with 13 cc. concd. H2SO4, kept 24 hrs. at room temp., poured onto crushed ice, neutralized with NH4OH, and extd. with Et2O gave 12.9 g. [3,4-(MeO)2C6H3]2CHCH2NH CH2Ph, b0.08 210-20°; HCl salt m. 111°. XXV (3.15 g.), 2.5 g. o-C6H4(OMe)2, and 3 cc. AcOH treated dropwise at 0° with 2.6 cc. concd. H2SO4, and the resulting oil kept 2 weeks and filtered gave 3.5 g. [3,4-(MeO)2C6H2]2CHCH2N(CH3Ph)2, m. 68-9°; HCl salt m. 122-3° (C6H6-ligroine). IX (5.1 g.) in 40 cc. dry C6H6 treated 1 hr. below 40° with BF3, kept 2 hrs. at room temp., treated a few min. with a stream of dry air and then with stirring with dry NH3, filtered, and distd. yielded 1.2 g. 2-methylindole (XXVIII), b0.4 93°, m. 59° (petr. ether). Similarly were prepd. the following substituted indoles [substituent(s), b.p./mm., m.p., % yield, and starting material given]: 2-Et, --, 45-6° (petr. ether), 35, XV; 2,7-di-Me (XXIX), 105°/1, 35° (petr. ether), 49, X; 2-ethyl-7-methyl, 112°/1, 29° (petr. ether), 48, XVI; 2,6-di-Me (XXX), 90°/1, 84° (petr. ether), 48, XI; 2-ethyl-6-methyl, 116°/1, 65° (petr. ether), 51, XVII; 2,5-di-Me (XXXI), 105°/0.3, 115° (petr. ether), 53, XII; 2-ethyl-5-methyl, 116-18°/1, 81° (petr. ether), 47, XVIII; 1,2-di-Me, --, 56° (petr. ether), 29, XXVI. p-MeC6H4NH2 (22 g.) and 16 g. VIII heated 7 hrs. at 120°, cooled, treated with 100 cc. 50% aq. NaOH, and extd. with

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Et2O yielded 2 g. XXXI, m. 115°. Similarly were prepd. XXX, m. 85°, 13%; XXIX, m. 35°, 13%; XXVIII, m. 59-60°, 10%. The ultraviolet absorption max. of the various indoles prepd. are tabulated.

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ORIGINAL REFERENCE NO.:	58:12493b-h,12494a-h,12495a-c
TITLE:	Arylamino acetals. Synthesis of indoles from phenylamino acetals
AUTHOR(S):	Chastrette, Maurice
CORPORATE SOURCE:	Fac. Sci., Paris
SOURCE:	Ann. Chim. (Paris) (1962), 7, 643-68
DOCUMENT TYPE:	Journal
LANGUAGE:	Unavailable
OTHER SOURCE(S):	CASREACT 58:73176

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AB Amine addition compds., effective in controlling hypertension, were prepared by heating a secondary or tertiary amine with a chloroacetylene to give amino acetylenes, which were catalytically hydrogenated to aminoethylenes and aminoethanes. Hydration of the aminoacetylenes gave amino ketones, from which the hydroxyamines were prepared by reduction Thus, 46 g. Na in small chunks was added with stirring to about 3 l. liquid NH3 while acetylene gas was passed into the liquid; after the bluish color had disappeared, 228 g. diisopropyl ketone was added, addition of C2H2 continued for about 4 hrs., 1 l. Et2O added, the mixture kept overnight, 1 l. H2O added, the Et2O layer separated, dried, and distilled in vacuo in the cold, and the residue distilled to give 3-isopropyl-4-methyl-1-pentyn-3-ol, b28 80-83°, n25D 1.442. Also prepared were 3-methyl-1-heptyn-3-ol, b14 62-3°, n25D 1.434, 3,4,4-trimethyl-1-pentyn-3-ol, b100 88-90°, n25D 1.438, and 3,4-dimethyl-1-hexyn-3-ol, b48 75°, n25D 1.435. Chloroacetylenes were prepared according to the method of Hennion and Maloney (CA 47, 478i): 3-chloro-3-methyl-1-butyne, b. 74-6°, n25D 1.416; 3-chloro-3-isopropyl-4-methyl-1-pentyne, b55, 92-7°, n25D 1.453; 3-chloro-3,4-dimethyl-1-hexyne, b32 67-77°, n25D 1.450; 3-chloro-3,4-dimethyl-1-pentyne, b52 54-55°, n25D 1.448; 3-chloro-3-methyl-1-heptyne, b28 64-68°, n25D 1.440; 3-chloro-3-methyl-1-hexyne, b45 54-55°, n25D 1.435; 3-chloro-3-ethyl-1-hexyne, b37 69-71°, n25D 1.443; 3-chloro-3,4-dimethyl-1-hexyne, b66 73-79°, n25D 1.454; 3-chloro-3,4,4-trimethyl-1-pentyne, b94 82°. Acetylenic amines were prepared by the method of Hennion and Nelson (CA 51, 12905h), to give the following substituted 3-methyl-1-butynes (substituent given): 3-isopropylamino, b. 115-18°, n25D 1.419, m. about 27° (HCl salt m. 204-6°, sulfate salt); 3-ethylamino, b. 108-9°, m. about 50.5° (HCl salt m. 183-5°, maleate salt); 3-propylamino, b. 129° (HCl salt m. 171-3°); 3-butylamino, b. 151°, m. 24°, n25D 1.428 (HCl salt m. 183-4°); 3-isobutylamino, b. 140-2°, m. about 19°, n25D 1.423 (HCl salt m. 215-16°); 3-sec-butylamino, b67 72°, n25D 1.425 (HCl salt m. 181-3°); 3-tert-butylamino, b84 72-2.5°, m. 24°, n25D 1.430 (HCl salt m. 221-3°); N,N-dipropyl-3-amino, b19 74°, n25D 1.436 (HCl salt m. 208-9°); 3-sec-amyl-amino, b. 66°, n25D 1.428 (HCl salt m. 133-5°); 3-tert-amylamino, b6 51°, n25D 1.437 (HCl salt m. 167-9°); 3-allylamino, b. 130° (HCl salt m. 194-5°); **N-methyl**-N-isopropyl-3-amino, b135 96-98°, n25D 1.435 (HCl salt m. 184-6°); **N-methyl**-N-tert-butyl-3-amino, b130 115-16°, n25D 1.450 (HCl salt m. 140-2°); N-ethyl-N-isopropyl-3-amino (HCl salt m. 177-9°). The following 3-substituted amino-3-methyl-1-pentynes (substituents given) were prepared): isopropyl, b93 77-7.5°, n25D 1.426 (HCl salt m. 196-7°); tert-butyl, b25 62°, n25D 1.435 (HCl salt m. 204-5°); isopropyl-4-methyl, b50 58-60 (HCl salt m. 179-81°); isopropyl-4,4-dimethyl, b104 110-30°, n25D 1.445 (HCl salt m. 198-9°); tert-butyl-4,4-dimethyl, b28 110-11°, n25D 1.457 (HCl salt m. 238°); tert-butyl-4-methyl, b58 96-8°, n25D 1.400 (HCl salt m. above 280°); ethyl-isopropyl (HCl salt m. 177-9°); methylisopropyl-4-methyl, b20 73-5°, n25D 1.445 (HCl salt m. 198-200°). The following 3-ethyl-1-pentynes (substituents given) were prepared: 3-isopropylamino, b25 71°, n25D 1.433 (HCl salt m. 222-3°); 3-tert-butylamino, b23 75°, n25D 1.440 (HCl salt m. 267-8°); 3-ethylamino, b70 77-9°, n25D 1.437 (HCl salt m. 205-7°); **N-methyl**

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-N-isopropyl-3-amino (HCl salt m. 143-5°). The following 3-methyl-1-hexynes (substituents given) were prepd.: 3-isopropylamino, b38 73.5-5.5°, n25D 1.432 (HCl salt m. 167-9°); 3-tert-butylamino, b8 50-3°, n25D 1.439 (HCl salt m. 175-6°); 3-ethylamino-5-methyl (HCl salt m. 204°); 3-tert-butylamino-4-methyl, b6 53°, n25D 1.447 (HCl salt m. 174-5°). The following 4-methyl-1-pentynes (substituents given) were prepd.: 3-isopropylamino-3-isopropyl, b52 110-18°, n25D 1.450 (HCl salt m. 206-7°); 3-ethylamino-3-isopropyl, b15 68-81°, b11 76-81°. Also prepd. were: 4-tert-butyl-amino-4-methyl-2-pentyne, b59 90-2°, n25D 1.440 (HCl salt m. 145-6°); 3-tert-butylamino-3-ethyl-1-hexyne, b8 68°, n25D 1.447 (HCl salt m. 163-4°); 3-tert-butylamino-3-methyl-1-heptyne, b10 76°, n25D 1.441 (HCl salt m. 144-6°). The following ethylenic amines were prepd.: substituted 3-methyl-1-butenes (substituents given): 3-isopropylamino, b. 121-2, n25D 1.417 (HCl salt m. 115-16°); 3-tert-butylamino (HCl salt m. 202-4°); **N-methyl**-N-isopropyl-3-amino, b107 76-80°, n25D 1.434; 3-ethylamino, b. 110°, n25D 1.416 (HCl salt m. 138-40°). 3-Ethyl-1-pentenes (substituents given): 3-tert-butylamino (HCl salt m. 183-4°); 3-ethylamino, b70 84°, n25D 1.436 (HCl salt m. 167-9°), 3-iso-propylamino, b50 89°, n25D 1.436 (HCl salt m. 196-8°). 3-Methyl1-pentenes (substituents given): 3-tert-butylamino, b25 67°, n25D 1.437 (HCl salt m. 164-6°); 3-isopropylamino-4-methyl (HCl salt m. 101-5°; 3-ethylamino, b110 77°, n25D 1.427 (HCl salt m. 114-17°; 3-isopropylamino, b90 84°, n25D 1.428 (HCl salt m. 116-17°). The following satd. amines were reported: 3-substituted 3-methylbutanes (substituents given): ethylamino, b. 112-15°, n25D 1.405 (HCl salt m. 160-1°); tert-butylamino, b61 74°, n25D 1.418 (HCl salt m. 218-19°); 3-sec-butylamino (HCl salt m. 137-9°); 3-sec-amylamino (HCl salt m. 142-4°); 3-tert-amylamino (HCl salt m. 183-5°); methylisopropylamino, b110 90° (HCl salt m. 142-4°); isopropylamino, b130 78-80°, n25D 1.408 (HCl salt m. 131-2°). 3-Substituted 3-ethylpentanes (substituents given): tert-butylamino (HCl salt m. 172-3°); isopropylamino (HCl salt m. 217-18°); ethylamino, b70 88°, n25D 1.427 (HCl salt m. 189-91°). 3-Substituted 3-methylpentanes (substituents given): isopropylamino-4-methyl (HCl salt m. 183-4°); isopropylamino-4,4-dimethyl (HCl salt m. 183-4°); ethylamino, b110 81°, n25D 1.419 (HCl salt m. 164-6°); isopropyl-amino, b90 87°, n25D 1.421 (HCl salt m. 194-6°); tert-butylamino, b25 70°, n25D 1.429 (HCl salt m. 195-6°). Also prepd. were: 3-etaylamino-3-isopropyl-4-methylpentane (HCl salt m. 195-6°); 3-isopropylamino-3-methylhexane (HCl salt m. 113-15°); 3-tert-butylamino-3-methylhexane (HCl salt m. 142-4°); and 2-tert-butylamino-2-methylpentane, b58 90-1°, n25D 1.423 (HCl salt m. 136-8°). The amino ketones, prepd. by hydration of the corresponding acetylenic **amine** with aq. H2SO4 and mercuric oxide as catalysts, were given as follows: 3-substituted 3-methyl-2-pentanones (substituents given): tert-butylamino (HCl salt m. 152-4°); isopropylamino (HCl salt m. 99-101°). 3-Substituted 3-ethyl-2-pentanones (substituents given): isopropylamino (HCl salt m. 135-6°); tert-butylamino (HCl salt m. 173-5°). 3-Substituted 3-methyl-2-butanones (substituents given): tert-butyl-amino, b58 104°, n25D 1.434 (HCl salt m. 208°); isopropylamino (HCl salt m. 131-3°). The amino alcs. were prepd. by NaBH4 redn. of the secondary or tertiary amino ketones in alc., or with LiBH4 in Et2O: 3-substituted 3-ethyl-2-pentanols (substituents given): isopropylamino

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(HCl salt m. 126-7°); tert-butylamino (HCl salt m. 141-2°). 3-Substituted 3-methyl-2-butanols (substituents given): tert-butylamino (HCl salt m. 154-6°); pyrrolidino, b17 99°, n25D 1.465; isopropylamino (HCl salt m. 125-7°). Also prepd. was 3-tert-butylamino-3-methyl-2-pentanol; HCl salt m. 126-7°.

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INVENTOR(S): Easton, Nelson R.; Kornfeld, Edmund C.
PATENT ASSIGNEE(S): Eli Lilly and Co.
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DOCUMENT TYPE: Patent
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PATENT INFORMATION:

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GB 921943			GB	

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AB Amidomethylated aromatic compds., Ar(CH2NHCOR)n, are prepared For example, 15.9 g. m-xylene, 35.0 g. **N-methylolacrylamide** (I), and 100 ml. 85% H3PO4 heated at 65-70° until the endothermic reaction subsides then at 85-90° 4 hrs, cooled, poured into stirred cold H2O, filtered, washed, and dried yields 76% crude 4,6-bis(acrylamidomethyl)-m-xylene. Replacing I by **N-methylolacetamide** yields 4,6-bis(acetamidomethyl)-m-xylene (II), m. 252-6°. From 22.5 ml. H2SO4, 105 ml. HOAc, and 71.5 g N, **N'-methylenediacetamide**, m 197-8° prepared from acetamide and **formaldehyde** in xylene at about 130°, heated 5.5 hrs. at 90° gives N-(2,4-dimethylbenzyl)acetamide, m. 113-12.5° (C6H6). Diacetamidomethyl ether (III), m. 97-98.5° (dioxane), is prepared from 418 g. acetamide (IV), 360 g. paraformaldehyde (V), and 1000 ml. xylene refluxed with vigorous stirring in a flask with a trap for H2O formed, until 121 ml. H2O is collected. Heating 65 g. III with 17 ml. H2SO4 and 78 ml. HOAc 5.5 hrs., cooling, and diluting with dilute NH4OH gives II. From 118 g. IV, 66 g. V, and 3 ml. 40% aqueous KOH heated 15 min. at 60% poured into 500 ml. HOAc plus 500 ml. Ac2O, heated 15 hrs. at 100° and **distilled** in vacuo is formed, after removal of excess reagents, N-(acetoxymethyl)acetamide (VI), b8 117-25°, n 1.4451. VI reacted with m-xylene, H2SO4, and HOAc 4 hrs. at 85-90° to give II. N-(Chloromethyl)acetamide, m-xylene, and anhydrous ZnCl2 refluxed about 3 hrs. and poured into dilute NH4OH gives N-(2,4-dimethylbenzyl)acetamide. A mixture of 496 g. II, 250 ml. H2SO4, and 2 l. H2O is refluxed with agitation 33.5 hrs., cooled, extracted with C6H6, the precipitate filtered off, and the aqueous layer neutralized with NaOH solution Continuous extraction with C6H6 5 hrs., with BuOH 4 hrs., removal of solvents, and purification gives 4,6-bis(aminomethyl)-m-xylene (VII), m. 139-40°. VII.2HCl, m. 305-10° in Tetralin treated with phosgene at 200-05° 5-7 hrs. gives after **distillation**, mainly 4,6-bis(isocyanato methyl)-m-xylene. The latter reacts with polyesters to form polyurethan resins.

ACCESSION NUMBER: 1962:455998 CAPLUS
DOCUMENT NUMBER: 57:55998
ORIGINAL REFERENCE NO.: 57:11099g-i,11100a-b
TITLE: Amidomethylation of aromatic compounds
INVENTOR(S): Parris, Chester L.
PATENT ASSIGNEE(S): Pittsburgh Plate Glass Co.
SOURCE: 5 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3024282		19620306	US	19571029
GB 891771			GB	

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AB N,N-Disubstituted 2-aminobutane-1,4-diols were prepared and subjected to ring closure to form 3-(N,N-disubstituted-amino)tetrahydrofurans, intermediates for quaternary ammonium compds. with neurophysiol. properties. Propargyl tetrahydropyranyl ether (81.5 g.) in absolute Et2O was treated at 0° with stirring with 37 g. BuLi or 49 g. PhLi in Et2O, the mixture stirred 2 hrs. at 0°, then stirred until room temperature was attained, the mixture added dropwise under N to a stirred solution of 100 g. (EtCO)2CO in absolute Et2O at -85° and left 14 hrs. to give γ-propionylpropargyl tetrahydropyranyl ether (I), b0.04 64-6°. I (24.6 g.) dissolved in absolute Et2O, treated with 10 ml. dry NHMe2, the mixture left for 14 hrs. at room temperature, excess NHMe2 and Et2O removed in vacuo, and the residue distilled in vacuo yielded γ-propionyl-β-dimethylaminoallyl tetrahydropyranyl ether (II), b0.02 110° (bath temperature), n. room temperature (AcOEt). II (29.2 g.) hydrogenated in AcOH in the presence of Pt, the mixture filtered, AcOH removed in vacuo, the residue extracted with Et2O and dissolved in water, the solution brought to pH 12 and extracted with Et2O, yielded a mixture of δ-hydroxy-β-dimethylamino-n-hexyl tetrahydropyranyl ether, δ-hydroxy-β-dimethylamino-n-hexanol, and their Ac derivs. The mixture (6.3 g.) was dissolved in 33 ml. sirupy H3PO4 (d. 1.7) and 100 ml. water, the solution heated 1 hr., brought to pH 14, and steam-distd., the distillate neutralized with N HCl, evaporated to dryness in vacuo, and the residue made alkaline and continuously extracted with Et2O, yielded 3-dimethylamino-5-ethyltetrahydrofuran, b10-11 602°. To 6.1 g. stirred and cooled 90% formic acid 3.8 g. dl-2,5-dimethyl-2,5-dihydroxy-3-aminohexane was added dropwise, followed by 4.22 g. 37% aqueous formaldehyde, the mixture heated to 95° for 12 hrs., cooled to 5°, 2 ml. concentrated HCl added dropwise, and the mixture evaporated to dryness in vacuo. The residue was dissolved in 40 ml. water, the solution treated with activated C, filtered, brought to pH >11 and continuously extracted with Et2O to yield dl-2,5-dimethyl-2,5-dihydroxy-3-dimethylaminohexane (III), b0.0025 60-5°. III (2 g.) treated at 0-10° with 4 ml. 33 volume-% H2SO4, the mixture heated 4 hrs. at 95°, diluted with 10 ml. water, brought to pH >11 and continuously extracted with Et2O yielded dl-2,2,5,5-tetramethyl-3-dimethylaminotetrahydrofuran, b11 56-7°.

ACCESSION NUMBER: 1961:131369 CAPLUS
DOCUMENT NUMBER: 55:131369
ORIGINAL REFERENCE NO.: 55:24791e-i
TITLE: Tertiary amines derived from tetrahydrofuran
INVENTOR(S): Eugster, Conrad H.; Denss, Rolf; Hafliger, Franz; Hofer, Bruno; Pfister, Rudolf; Zimmermann, Markus
PATENT ASSIGNEE(S): J. R. Geigy Akt.-Ges.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CH 349615		19601215	CH	

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AB cf. CA 46, 4490h; 53, 9086i; 55, 19814b. In order to obtain detailed information concerning the structures of the intermediates in carbonium ion type interconversions of the title compds., the extent of isotope-position rearrangement in the reactions of cyclopropylcarbinylamine-α-C14 (I) with HNO2 and cyclopropylcarbinol-α-C14 (II) with Lucas reagent was investigated. Cyclopropylmagnesium bromide was carbonated with C1402 and the acid (III) converted to the amide, which was reduced to I. II was prepared by LiAlH4 reduction of III. The studies showed that the 3 CH2 groups in the starting material achieved a high degree of equivalence between reactants and products. This was best reasoned by assuming a rapid equilibrium of 3 isomeric nonclassical unsymmetrical bicyclobutonium ion intermediates. The degradation of allylcarbinyl-α-C14 chloride (IV) was done by treating 6.9 g. IV with 50 ml. 87% HCO2H (V) and 17.0 g. 30% H2O2. The mixture was stirred at 50° until clear (30 min.), then stirred 2 hrs., V removed in vacuo, and methanolic HCl added to the residue. The mixture was refluxed 1 hr., HCO2Me and MeOH removed, and 6.1 g. 4-chloro-1,2-butanediol-α-C14 (VI), n25D 1.4760, distilled, b0.8 117°, n25D 1.4735. Hydrolysis of the intermediate formate with KOH gave 3-hydroxytetrahydrofuran, b7 61-2°, n25D 1.4396; phenyl carbamate m. 117.2-17.6°. VI (0.66 g.), 1.13 g. NaIO4, and 50 ml. H2O left 2 hrs. at room temperature, extracted with Et2O, and the aqueous layer added to 0.74 g. methone in 200 ml. H2O gave 0.38 g. formaldehyde-C14 dimethone, m. 191.6-2.6°. IV (4.66 g.) was converted into the Grignard reagent (1.44 g. Mg in 20 ml. Bu2O) and treated with 6.0 g. H2SO4 in 20 ml. H2O, the resulting 1-butene heated at 110° with 30 ml. 87% V and 11.3 g. 30% H2O2 and worked up to give 1,2-butanediol-α-C14 (VII), b12 90°, n25D 1.4396; bis(phenylcarbamate) m. 116-17°. A mixture of 0.516 g. VII and NaIO4 was treated as before, continuously extracted with Et2O, and the aqueous layer found to contain formaldehyde 84% dimethone. The Et2O extract was stirred with 0.98 g. NaMnO4.3H2O, 0.12 g. NaOH, and 25 ml. H2O for 30 min., filtered, decolorized with NaHSO3, and the Et2O removed. The aqueous layer was treated with 30 g. Na2SO4, and steam distilled until 300 ml. distillate was collected. The distillate was neutralized with NaOH, evaporated, and 0.87 g. salt obtained. A portion was converted to the p-bromophenacyl propionate-α-C14, m. 61.4-2.8°, and the remainder treated with 0.6 ml. H2SO4 and 0.0028 mole NH3 in CHCl3 at 50° to analyze the gas for C14 (as BaI4CO3), and the acid-CHC13 mixture treated with p-BrC6H4SO2Cl to give 76% N-ethyl- and 24% N-methyl-p-bromobenzenesulfonamide. Deamination of I was accomplished by the method of R. and M. (CA 46, 1453a). The deamination products were degradated by treating KMnO4 and identifying the oxidation products. Degradation of cyclobutanol-α-C14 was also studied in order to assure the reliability of the methods of degradation.

ACCESSION NUMBER: 1961:118139 CAPLUS
DOCUMENT NUMBER: 55:118139
ORIGINAL REFERENCE NO.: 55:22160c-i,22161a
TITLE: Small-ring compounds. XXIII. The nature of the intermediates in carbonium ion-type interconversion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives
AUTHOR(S): Mazur, Robert H.; White, William N.; Semenow, Dorothy A.; Lee, C. C.; Silver, Mare S.; Roberts, John D.
CORPORATE SOURCE: California Inst. of Technol., Pasadena
SOURCE: Journal of the American Chemical Society (1959), 81, 4390-8

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CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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GI For diagram(s), see printed CA Issue.

AB The peroxide obtained by Girsewald and Siegens (CA 15, 2416) from N2H4, HCHO, and H2O2, and claimed to be CH2.O.O.CH2.NN:CH2, actually had twice this mol. weight both in PhNO2 and in dioxane, and had the structure I. The O in I and other cyclic peroxides was determined iodometrically. EtNH2 (0.05 mol) and 0.1 mol HCHO (30% in H2O) cooled and treated with 2.5 cc. AcOH and then with 7 cc. 30% H2O2 gave 2 g. (C4H9NO2)n, viscous oil, whose cryoscopic mol. weight in C6H6 was approx. 610. N,N'-Dimethylolurea (1.2 g.) (m. 130°) in 25 cc. H2O, 10 cc. 30% H2O2, and 10 cc. concentrated HNO3 gave 0.34 g. (C3H6N2O3)n, m. 185-7° (decomposition), insol. in all organic solvents and identical with the compound made from urea by the method of G. and S. (loc. cit.). Difficulties in accepting a monomeric structure were discussed. (MeNH)2.2HCl (5 g.) cooled and treated 2 h. with 3.3 g. NaOH in 15 cc. H2O and 4 cc. 40% HCHO, saturated with K2CO3, and extracted with Et2O gave 1.56 g. 1,2,4,5-tetramethylhexahydro-sym-tetrazine (II), b11 58-60°, n20D 1.4695; picrate m. 115-16.5° (EtOH). Formed similarly was 10% tetraisopropyl homolog of II, m. 57-8° (petr. ether), camphorlike odor. (MeNH)2.2HCl (5 g.) and 3.63 g. Me2NNH2.2HCl was cooled and treated with 5 g. NaOH in 20 cc. H2O, followed by 8 cc. 40% HCHO, to give on Et2O extraction 1.35 g. II. A similar mixture of these amine salts with aqueous NaOH and HCHO (as above) was added dropwise to 100 g. solid NaOH and distilled to give 93% N-methylene-N',N'-dimethylhydrazine, b760 71-2°, n20D 1.4312 (Klages, et al., CA 35, 4345g). o-C6H4.CH2.CH2.N.NMe.CH (isohydrazone) (5 g.) was refluxed in 25 cc. 2N H2SO4, the mixture cooled, and extracted with Et2O. The aqueous phase at 0° was treated successively with 5 cc. 40% HCHO, 5 cc. perhydrol, and 25 cc. 3.5N AcONa to give at 0° 4.7 g. III, m. 71-1.5° (decomposition) (petr. ether); picrate m. 91-3°, which with NH3 and ether was reconverted to III. The following reactions were carried out at 0°. (MeNH)2.2HCl (5.35 g.) in 40 cc. 3.4N AcONa was treated 5 min. with 8 cc. 40% HCHO and 4 cc. 30% H2O2, the mixture kept 5 min. without cooling then cooled to 0°, saturated with AcOK.AcOH (m. 148°) [Melsens, Ann. 52, 274(1844)], extracted 4 times with Et2O, these exts. combined and extracted with saturated Na2SO4, the dried Et2O solution at 0° shaken with active C, filtered, and evaporated in vacuo under anhydrous conditions to give CH2.NMe.NMe.CH2.O.O (IV), pale yellow oil, crystallizing when cooled with dry ice, m. -20° (pentane). IV treated with 1-methyl-6,8-dinitro-2-ethoxy-1,2-dihydroquinoline in AcOH gave 70% bis(1-methyl-6,8-dinitro-1,2-dihydro-2-quinolyl) peroxide, decomposed at 120-24° (previously given as 128°). IV with tetrahydrophthalazine-HCl in an acetate-buffered solution gave di(o-xylylene)hexahydrotetrazine (CA 54, 14263c). Formed similarly to IV were 64% N, N'-diethyltetrahydro-4,5-dioxapyridazine, m. 26°, n20D 1.4438, and 52% N,N'-diiso-Pr homolog, m. -1 to 2° (pentane). 26 refs.

ACCESSION NUMBER: 1961:8158 CAPLUS
DOCUMENT NUMBER: 55:8158
ORIGINAL REFERENCE NO.: 55:1644i,1645a-g
TITLE: Cyclic peroxides from hydrazine derivatives
AUTHOR(S): Schmitz, Ernst
CORPORATE SOURCE: Deut. Akad. Wiss., Berlin-Adlershof
SOURCE: Ann. (1960), 635, 73-82
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB The preparation was described of diquaternary compds., which were ganglion-blocking agents. Acetophenone (12 g.), 4.5 g. paraformaldehyde, and 14.2 g. methyl(2-piperidinoethyl)-amine (I) in 30 cc. absolute EtOH acidified to Congo red with concentrated HCl, refluxed 1 hr., 3 g. paraformaldehyde added, the solution refluxed 2 hrs., and the cooled solution diluted with Me2CO precipitated 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-propanone-2HCl (II), needles, m. 201-2° (MeOH); free base prepared by treatment with aqueous alkali and extraction with Et2O. 2-Bromopyridine (15.8 g.) in 20 cc. Et2O added with stirring in an atmospheric of dry N to a solution of BuLi from 1.75 g. Li and 10 g. BuCl at -60°, an anhydrous solution of the free base from 10 g. II added after 5 min., the temperature allowed to rise to -20° during the next 30 min., the product added to ice, the mixture acidified with HOAc, the aqueous phase washed with Et2O, made alkaline with NaOH, extracted with Et2O, and the extract evaporated yielded 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-pyridyl)-1-propanol (III), light brown oil, b0.05 190-5°; oxalate m. 201° (EtOH). III (5 g.) in 15 cc. 85% H2SO4 heated on the steam bath 15 min., the cooled solution diluted with H2O, basified with aqueous NH3, and extracted with petr. ether gave on evaporation of the extract 3.5 g. 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-pyridyl)-1-propene (IV), dark brown oil. IV (3.5 g.) in 50 cc. HOAc shaken under H at 50°/1 atmospheric with 1 g. 3% Pd-C until 250 cc. H was absorbed, the filtered solution diluted with H2O, made alkaline with aqueous NH3, and extracted with Et2O gave on evaporation of the extract 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-pyridyl)propane (V), b0.05 164-5°; oxalate m. 188°. MeI (1.6 g.) added to 2 g. V in 15 cc. MeOH precipitated after 16 hrs. N1,N1,N2-trimethyl-N1-[3-phenyl-3-(2-pyridyl)propyl]ethylene-1-ammonium-2-piperidinium diiodide (VI), cream-colored needles, m. 179° (MeOH). The dried Et2O solution of the free base from 40 g. II added during 5 min. to a cooled stirred solution of 2-thienyllithium (from 33.6 g. thiophene, 0.4 mole BuLi, and 200 cc. Et2O), stirring continued 30 min. in the cold, and the mixture poured on ice gave 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)-1-propanol (VII), pale yellow oil, b0.15 220°; oxalate decomposed at 190°. VII (10 g.) and 100 cc. 2N HCl kept 18 hrs. at room temperature, NaOH solution added, and the oil extracted with Et2O gave 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)propene (VIII), pale yellow oil, b0.1 176-80°; oxalate m. 208°. VIII treated as in the preparation of VI gave N1-[3-phenyl-3-(2-thienyl)prop-2-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-piperidinium diiodide, m. 195° (MeOH). KOH (92.5 g.) in 90 cc. H2O added to 690 g. 1,5-dibromopentane, 141 g. phenol, and 500 cc. EtOH, the mixture refluxed 2 hrs., the solvent removed in vacuo, H2O added to precipitate a heavy oily layer, the latter separated, washed with H2O, dried, and distilled yielded 1-bromo-5-phenoxypentane (IX), b15 176-8°. NaCN (96 g.) in 100 cc. H2O added to 400 g. IX in 400 cc. EtOH, the mixture refluxed 2 hrs., the solvent evaporated, and the product isolated with Et2O gave 1-cyano-5-phenoxypentane (X), b14 196-8°. X (96 g.) in anhydrous Et2O (200 cc.) added to a solution of PhLi (from 22.8 g. Li and 234 g. PhBr in 1000 cc. Et2O). the solution refluxed 2 hrs., the cooled solution poured on ice, acidified, and steam distilled yielded 6-phenoxy-1-phenyl-1-hexanone (XI), b0.2

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175°, needles, m. 55° (petr. ether). XI (35 g.) and 400 cc. HBr (d. 1.5) boiled 24 hrs. so that 200 cc. of the acid distilled through a column, the cooled residue poured into H2O, partially neutralized with NaOH, extd. with Et2O, the ext. washed with H2O and NaOH soln., and evapd. gave 6-bromo-1-phenyl-1-hexanone (XII), b0.05 124°, m. 33-5°. XII (15 g.) and 10 g. I warmed on the steam bath 1 hr., the cooled soln. dissolved in dil. HCl, the soln. washed with Et2O, made alk. with NaOH, extd. with Et2O, and the ext. evapd. gave 6-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-hexanone (XIII), b0.15 170°; oxalate m. 215°. XIII treated with 2-thienyllithium as in the prepn. of VII gave 6-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)-1-hexanol (XIV), b0.08 215-20°; oxalate, prisms, decompd. at 178-80° (EtOH). XIV (5 g.) in 25 cc. CHCl3 slowly satd. with HCl gas, kept 1 hr. at room temp., and the dried soln. evapd. at low temp. yielded 6-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)-1-hexene-2HCl (XV), hygroscopic needles, decompd. at 210° (EtOH-EtOAc); oxalate, prisms, m. 175° (EtOH). Refluxing XV in MeOH soln. with MeI pptd. on addn. of EtOAc N1-[6-phenyl-6-(2-thienyl)hex-5-enyl]-N1, N1, N2-trimethylethylene-1-ammonium-2-piperidinium diiodide, m. 161-3°. Et acrylate (50 g.), 71 g. I, and 50 cc. EtOH refluxed 8 hrs. gave Et β-[methyl(2-piperidinoethyl)amino]propionate (XVI), b15 161°. XVI treated with thienyllithium in the usual way gave 3-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-propanol (XVII), b0.1 184-8°; oxalate decompd. at 193°. XVII dehydrated as in the prepn. of XV gave 3-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-propene (XVIII); hydrochloride, prisms, m. 218° (EtOH); oxalate, prisms, m. 202° (80% EtOH). Refluxing with MeI in MeOH gave N1-[3,3-di(2-thienyl)prop-2-enyl]-N1, N1, N2-trimethylethylene-1-ammonium-2-piperidinium diiodide (XIX), needles, m. 183-4° (MeOH). The following compds. were prepd. similarly to the prepn. of XVII-XIX: 3-[methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-propanol, pale yellow oil, b0.05 180° (oxalate decompd. at 182°); 3-[methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-propene (XX) (oxalate m. 212-13°); N1-[3,3-di(2-thienyl)prop-2-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-pyrrolidinium diiodide, m. 168° (EtOH); 3-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-propanol, light yellow oil, b0.05 165° (oxalate decompd. at 172°); 3-[N-(2-diethyl-aminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-propene (XXI) [oxalate, prisms, m. 205° (90% EtOH)]; and N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[3,3-di(2-thienyl)prop-2-enyl]ethylene-1,2-diammonium diiodide, needles, m. 172° (EtOH). Acrylonitrile (24 g.) added slowly to 66 g. 3-morpholinopropylamine and the mixt. kept overnight at room temp. gave 2-cyanoethyl(3-morpholinopropyl)amine (XXII), b15 180°. Formaldehyde (30 cc. 40%) added to 70 g. XXII in 35 cc. 90% HCO2H, the mixt. heated 4 hrs. on the steam bath, NaOH soln. added, and the oil which sepd. pyrolyzed 3 hrs. at 270° gave methyl(3-morpholinopropyl)amine (XXIII), b12 100%, n22D 1.4715. XXIII treated as in the prepn. of XVII-XIX gave: 3-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-propanol, b0.05 200-2°, m. 77° (petr. ether) (oxalate m. 192-3°); 3-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-propene-2-HCl, decompd. at 233-4° (oxalate decompd. at 205-6°); and N1-[3,3-di(2-thienyl)prop-2-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-3-morpholinium diiodide, m. 184°. Et 6-bromohexanoate (20 g.) and 20 g. I warmed to 60° until reaction set in and the temp. rose spontaneously to 80°, the mixt. heated 2 hrs. on the steam bath after the reaction subsided, cooled, acidified, the acid soln. washed with Et2O, basified at 0° with aq. NH4, extd. with Et2O, and the ext.

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evapd. gave Et 6-[methyl(2-piperidinoethyl)-amino]hexanoate (XXIV), b0.05 130°. XXIV treated as in the prepn. of XVII-XIX yielded: 6-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-hexanol (XXV), b0.05 205°; 6-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-hexene, b0.1 180° [oxalate decompd. at 186° (EtOH)]; and N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-piperidinium diiodide, leaflets, m. 163° (EtOH). 6-[Methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-hexanol (XXVI), b0.05 205-10°, was prepd. by the method for prepn. of XXV. Oxalic acid (5 g.) in 20 cc. EtOH added to a hot soln. of 5 g. XXVI in 150 cc. EtOH and the slurry heated 5 min. on the steam bath pptd. the oxalate, decompd. at 200°, of 6-[methyl(2-pyrrolidinoethyl)amino]1,1-di(2-thienyl)-1-hexene, converted as in the prepn. of XIX to N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-pyrrolidinium diiodide, platelets, m. 97° (EtOH). 6-[N-(2-Diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-hexanol (XXVII), pale yellow oil, b0.08 194-6°, was prepd. by the method of prepn. of XXV. XXVII was converted as in the prepn. of XVIII and XIX to 6-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-hexene (XXVIII), b0.05 169-71 [picrate, needles, m. 153° (EtOH)], and N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[6,6-di(2-thienyl)hex-5-enyl]ethylene-1,2-diammonium diiodide, plates, m. 115° (EtOH). The following series of compds. was similarly prepd.: 6-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-hexanol, m. 66° (petr. ether); 6-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-hexene (hydrochloride m. 210-12°; oxalate decompd. at 191-3°); and N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethyltrimethylene-1-ammonium-3-morpholinium diiodide, hygroscopic powder. 6-[Methyl(2-morpholinoethyl)amino]-1,1-di(2-thienyl)-1-hexanol (XXIX), b0.1 220°, was prepd. by the method of prepn. of XXV. XXIX was converted by the methods used in the prepn. of VIII and VI into 6-[methyl(2-morpholinoethyl)amino]-1,1-di(2-thienyl)-1-hexene, b0.1 205° [oxalate, needles, decompd. at 192-3° (EtOH)], and N1-[6,6-di(2 thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-morpholinium diiodide, platelets, decompd. at 199° (EtOH). Na (20 g.) added portionwise during 30 min. to 7 g. XX in 400 cc. boiling PrOH, the mixt. boiled 2 hrs. longer, the soln. evapd. in vacuo, 500 ml. H2O added, and the soln. extd. with Et2O yielded on evapn. of the ext. methyl(2-pyrrolidinoethyl)[3,3-di(2-thienyl)propyl]amine (XXX), b0.03 160-2°; oxalate, prisms, decompd. at 200-1° (EtOH). XXX treated as in the prepn. of VI yielded N-[3,3-di(2-thienyl)propyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-pyrrolidinium diiodide, needles, m. 211° (EtOH-MeOH). The following compds. were similarly prepd.: methyl(2-diethylaminoethyl)[3,3-di(2-thienyl)propyl]amine, b0.05 155°, from XXI; N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[3,3-di(2-thienyl)propyl]ethylene-1,2-diammonium diiodide, needles, m. 213° (EtOH); methyl(2-diethylaminoethyl)[6,6-di(2-thienyl)hexyl]amine, b0.05 165°, from XXVIII [oxalate, prisms, m. 149° (EtOH)]; and N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[6,6-di(2-thienyl)hexyl]ethylene-1,2-diammonium diiodide, m. 191°. The following series of compds. were prepd. by methods similar to those used in the prepn. of XVII-XIX: 5-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-pentanol, b0.01 162-6°; 5-(N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-pentene, b0.01 170° (oxalate m. 150°); N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[5,5-di(2-thienyl)pent-4-enyl]ethylene-1,2-diammonium diiodide, m. 130°; 5-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-pentanol, b0.1 215-20°; 5-[methyl(3-

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morpholinopropyl)amino]-1,1-di(2-thienyl)-1-pentene (hydrochloride m. 234-7°; oxalate decompd. at 212-13°); and N1-[5,5-di(2-thienyl)pent-4-enyl]-N1,N1N2-trimethyltrimethylene-1-ammonium-3-morpholinium diiodide, m. 115-17°.

ACCESSION NUMBER: 1960:97715 CAPLUS
DOCUMENT NUMBER: 54:97715
ORIGINAL REFERENCE NO.: 54:18567b-i,18568a-i,18569a-f
TITLE: Diquaternary compounds
INVENTOR(S): Coker, Geoffrey G.
PATENT ASSIGNEE(S): Wellcome Foundation Ltd.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 830519		19600316	GB	

L14 ANSWER 25 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB cf. C.A. 52, 7319h. The title compound is made in an eight-step synthesis. Anisoin (50 g.) 128 g. hydrated SnCl2, 120 cc. concentrated HCl, and 125 cc. EtOH are heated on steam bath 2 hrs. The precipitate is filtered off and washed with dilute HCl and water to yield deoxyanisoin (I), m. 109°. To 6.5 g. freshly activated powdered Zn is added iodine and 15 cc. of a solution of 12.8 g. I and 16.7 g. BrCH2CO2Et in 25 cc. benzene and 25 cc. toluene. The mixture is heated with stirring until it reacts and then cooled. The rest of the solution is added, the mixture heated 2 hrs., 100 cc. 10% H2SO4 added, the organic layer washed with 5% H2SO4, 10% NaHCO3, and water, and dried. The solvent is evaporated in vacuo and the residue distilled at 280°/23 mm. to give, with dehydration during distillation, 7 g. Et β,γ-bis(4-methoxyphenyl)butenoate (II), m. 78°. II (7 g.) is saponified with 20% KOH in EtOH to yield 6 g. free acid (III), m. 180° (EtOH); S-benzylisothiuronium salt m. 174° (EtOH). (III) 6 g. reduced by 300 g. 3% Na-Hg yields EtOH, 5 g. β,γ-bis(4-methxoyphenyl)butyric acid (IV), m. 167°; S-benzisothiuronium salt m. 132° (MeOH). Dry NH3 is passed in a melt of 6 g. IV at 200-30° for 1.5 hrs., the liquid poured into benzene and the precipitate recrystd. from EtOH to yield 4.5 g. β,γ-bis(4-methoxyphenyl)butyramide (V), m. 165°. V (6 g.), suspended in 30 cc. dioxane, is added to 100 cc. cold NaOCl, prepared by passing Cl through 10% NaOH. The mixture is held 2 hrs. at 70-5°, 15 g. KOH added, the mixture held 0.5 hr. at 80-5°, and cooled. 2 hrs. The product is extracted with benzene, and the extract worked up to give 2.5 g. β,γ-bis(4-methoxyphenyl) propylamine (VI), b28 194-7°; picrate m. 224° (EtOH). To 0.8 cc. of 40% formaldehyde in 5 cc. EtOH is added 1.3 g. VI. The mixture is heated on a water bath to remove EtOH and then cooled. The Schiff base is obtained as a paste, and the supernatent liquid removed by decantation. To the Schiff base is added 7 cc. 24% HCl with stirring, and the mixture is heated on water bath 0.5 hr. It is evaporated to dryness, and NH4OH is added. The precipitate is filtered off, washed with water, and recrystd. from EtOH to give 0.8 g. 4-(4-methoxybenzyl)-7-methoxy-1,2,3,4-tetrahydroisoquinoline (VII), m. 64°; picrate m. 264° (EtOH). VII (0.25 g.) treated with 10% 0.2 g. Pd-C gave 4-(4-methoxybenzyl)-7-methoxyisoquinoline; picrate m. 199° (EtOH).

ACCESSION NUMBER: 1959:51157 CAPLUS
DOCUMENT NUMBER: 53:51157
ORIGINAL REFERENCE NO.: 53:9223f-i,9224a-b
TITLE: Syntheses of isoquinoline derivatives of pharmacological interest. II. Synthesis of 4-(4-methoxybenzyl)-7-methoxyisoquinoline
AUTHOR(S): Deshpande, V. N.; Nargund, K. S.
CORPORATE SOURCE: Karnatak Univ., Dharwar, India
SOURCE: Journal of the Karnatak University (1957), 2(No. 1), 14-18
CODEN: JKAUAR; ISSN: 0453-3348
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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GI For diagram(s), see printed CA Issue.
AB Antipyretic, analgesic N-methylsulfonates or N-methylsulfinates of 1,2-dimethyl-3-phenyl-4-aminopyrazol-5-one are less toxic than the corresponding salts of 1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one used hitherto and are prepared by treating compds. of general formula O:C.NMe.NMe.CPh:C.NXR (I), where X is H and R is H, alkyl or aralkyl, with formaldehyde bisulfite or sulfoxalate. Instead of preformed H2C(OH)SO3Na, either HCHO and NaHSO3 in any order or HCHO plus H2SO3 with subsequent neutralization may be used. Thus, a mixture of 38% NaHSO3 solution 27.4 and 30% HCHO 10 is heated to 50° and I (R = X = H) (II) 20.3 parts added. After total dissolution and evaporation to dryness in vacuo, the residue is crystallized from dilute EtOH giving I (R = H, X = CH2SO3Na) (III), m. 194-6°. II reacts with isopropyl bromide to form 1,2-dimethyl-3-phenyl-4-isopropylaminopyrazol-5-one (IV), m. 91°. Replacing II by IV 24.5 parts in the above gives I (R = iso-Pr, X = CH2SO3Na) (V), m. 159°. Reduction of a mixture of II and isobutyraldehyde yields 1,2-dimethyl-3-phenyl-4-isobutylaminopyrazol-5-one (VI), m. 75°. Substituting VI 25.9 parts for II in the above produces I (R = iso-Bu, X = CH2SO3Na), m. 231°. 1,2-Dimethyl-3-phenyl-4-benzylideneaminopyrazol-5-one (VII) is reduced catalytically to 1,2-dimethyl-3-phenyl-4-benzylaminopyrazol-5-one (VIII), m. 90°. Using VIII 29.3 parts instead of II in the above method gives I (R = PhCH2, X = CH2SO3Na), m. 205°. When VII is melted with Me2SO4, water added, and the BzH formed distilled, 1,2-dimethyl-3-phenyl-4-methylaminopyrazol-5-one (IX), m. 130°, is obtained. Replacing II by IX 21.7 parts in the method given leads to I (X, R = Me, X = CH2SO3Na), m. 98°. An aqueous solution of IX 21.7 is stirred for some time with 30% HCHO 10, and 38% NaHSO3 solution 27.4 parts then added, and stirring continued at 40° for 1 hr. Evaporation and crystallization as above gives X, m. 98°. The NaHSO3 solution may also be added to the amine first, stirring in the formalin later at 40°. When SO2 6.4 is passed into a cooled solution of IX 21.7 in EtOH 100 plus 30% alc. HCHO 10 parts and the solution stirred for a further 15 min. and cooled, crystals of I (R = Me, X = CH2SO3H) (XI) are precipitated and filtered off. XI 31.1 is added to a suspension of CaCO3 5 in water 100 parts and after evolution of all the CO2, the solution is filtered, concentrated in vacuo and the Ca salt of XI precipitated out with EtOH, decompose 304°. IX 21.7 is added to a solution of formaldehydesulfoxalate 15.2 in water 25 parts at 40-50°. The solution formed is evaporated to dryness in vacuo and unreacted starting material extracted with Me2CO, leaving the I (R = Me, X = CH2SO2Na), decompose 221°. III 33.7 and Na2CO3 6 are dissolved in water 100 and warmed with stirring to 40° with diisopropyl sulfate 20 parts till evolution of CO2 ceases. The solution is evaporated in vacuo and the residue crystallized from dilute EtOH, giving V, m. 159°.

ACCESSION NUMBER: 1958:113805 CAPLUS
DOCUMENT NUMBER: 52:113805
ORIGINAL REFERENCE NO.: 52:20200b-h
TITLE: Salts of acid derivatives of 1,2-dimethyl-3-phenyl-4-aminopyrazol-5-one
INVENTOR(S): Ehrhart, Gustav; Krohs, Walter
PATENT ASSIGNEE(S): Farberke Hoechst AG vorm. Meister Lucius & Bruning
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1

L14 ANSWER 26 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 927992		19550523	DE	

L14 ANSWER 27 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB Methyltetrahydrofurfurylamine (I) (a new substance) is claimed in its preparation and use as solvent of poly(vinyl chloride). The Schiff base of tetrahydrofurfurylamine with formaldehyde is hydrogenated (with or without solvent) at 60-80° in the presence of Raney Ni and 60-120 atmospheric and the mixture distilled to give 80-85% I, b. 152-3°. Poly(vinyl chloride) is added to I, warmed at 45° for 1 hr., cooled to 18°, and kept 2 hrs. Data on the viscosity of 10-12% solns. are reported. The solns. are spun as usual, the coagulation bath being H2O or, better, a I aqueous solution (the enrichment of I in the bath should not surpass the concentration of 75%; best concentration 20%).

ACCESSION NUMBER: 1958:98023 CAPLUS
DOCUMENT NUMBER: 52:98023
ORIGINAL REFERENCE NO.: 52:17287h-i,17288a
TITLE: Chemical compound for preparing viscous solutions of poly(vinyl chloride)
INVENTOR(S): Siclari, Francesco; Bellano, Angelo
PATENT ASSIGNEE(S): SNIA VISCOSA Societa Nazionale Industria Applicazioni Viscosa S.p.A.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
IT 510118		19550120	IT	

L14 ANSWER 28 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB cf. C.A. 51, 7343b. [Throughout this abstract R = Me3C and R' = tert-C8H17.] The following imines were prepared by condensation of the appropriate amine with a ketone or aldehyde (b.p./mm. or m.p., and n20D given): CH2:N R, 65°/740, 1.4151; CH2:NR', 50-2°/13, 1.4381; PhCH:NR, 90-2°/11, 1.5211; p-O2NC6H4CH:N R, 73-5° (petr. ether), -; p-O2N C6CH:NR', -(noncrystallizable oil), 1.5430; p-O2NC6H4CH:NCHMe2 (I), 54-5°, -; p-O2NC6H4CH:NEt, 75-6°, -; iso-PrCH:NR, 51-3°/83, 1.4078; iso-PrCH:NBu, 67°/68, 1.4151; iso-PrCH:NCHMePh, 68°/0.8, 1.4975; iso-BuMeC:NPr, 65°/22, 1.4272; (RN:CH2)2(II), 52-3°, -; BuEtCHCH:NBu, 87°/8, 1.4338; 2-C5H4NCH:NR, 56-8°/0.2, 1.5335; PhCH:NR' (III), 100°/0.4, 1.5162; iso-PrMeC:NPr, 48°/26, 1.4230; EtMeC:NCH2CH:CH2, 94°/100, -; Et2C:NEt, 52-4°/54, 1.4230; Me2C:NC6H13, 53-5°/5.0, 1.4319; iso-PrCH:NCH2CHMe2, 57°/64, 1.4097; Et2C:NCHMePh, 64°/0.2, 1.5050. CH2Cl2 (100 cc.) treated with stirring with 30.0 cc. 50% H2O2 and 2 drops H2SO4 and then dropwise with cooling during 0.5 h. with 135 g. Ac2O, stirred 15 min. at 0° and 30 min. at room temperature, added dropwise during 0.5 h. with stirring to 85 g. CH2:NR in 100 cc. CH2Cl2, kept at room temperature overnight, washed, dried, and fractionated gave 46.4 g. 2-tert-butyloxazirane (IV), b75 52-4°, n20D 1.4150, containing 93.8% active O (determined with KI and AcOH). PhCH:NR (V) (80.5 g.) in 100 cc. CH2Cl2 treated dropwise with stirring with 15 cc. 90% H2O2, 50 cc. CH2Cl2, and 1 drop H2SO4 in 67.2 g. Ac2O and worked up after standing overnight yielded 63.1 g. 3-Ph derivative (VI) of IV, b0.3 61-3°, n20D 1.5081, containing 95.6% active O. CH2Cl2 (100 cc.), 25.3 cc. 90% H2O2, 2 drops H2SO4, and 114 g. Ac2O added dropwise to 71 g. II in 75 cc. CH2Cl2, kept overnight, and worked up gave 40 g. (crude) bis(2-tert-butyloxazirane), m. 53-6° (petr. ether at -78°), which chromatographed on silica gel gave material, m. 82-4° (presumably meso), and a 2nd fraction, m. 42-3° (presumably dl). Similarly were prepared the following substituted oxaziranes (substituents in 3, 3, and 2-positions, % yield, b.p. or m.p., mm., active O, and n20D given): H, H, R' (VII), 69, 70-2°/6, 99.2, 1.4445; Ph, H, R', 67, -, -, 1.5019; p-O2NC6H4, H, iso-Pr, 60, 46-8°, 92.0, -; p-O2NC6H4, H, Et, 97, 34-5°, 99.3, -; p-O2NC6H4, H, R, 78, 65-6°, 99.4, -; iso-Pr, H, R (VIII), 71, 68-70°/39, 99.8, 1.4152; iso-Pr, H, Bu (IX), 65, 65-7°/10, 91.5, 1.4178; BuEtCH, H, Bu, 83, -, 98.7, 1.4350; iso-Pr, H, CHMePh (X), 80, -, 99.7, 1.4956; iso-Bu, Me, Pr (XI), 73, 61°/8, 93.6, 1.4267; p-O2NC6H4, H, R', 66, 54-6°, 96.9, -; Me, iso-Pr, Pr, 64, 60°/15, 94.7, 1.4222; Bu, H, H, 74, 43°/20, 98.1, 1.4178; iso-Pr, H, R', 78, -, 99.6, 1.4385; Me, Et, CH2CH:CH2, 59, 51°/6, 91.2, 1.4413; Et, Et, Et (XII), 56, 62°/19, 97.7, 1.4225; Me, Me, C6H13, 14, 58°/3, 94.7, 1.4278; iso-Pr, H, iso-Bu (XIII), 50, 53°/12, 92.0, 1.4150; Et, Et, MePhCH (XIV), 91, -, 90.1, 1.5038; 2-pyridyl, H, R, 75, 68-70°/0.4, 96.1, 1.5010. CH2Cl2 (50 cc.), 9.8 cc. 90% H2O2, 1 drop H2SO4, and 44.1 g. Ac2O added with stirring to 45.9 g. N-cyclohexylideneisobutylamine in 50 cc. CH2Cl2 gave 41.1 g. 2-isobutyl-3,3-pentamethyleneoxazirane (XV), b1.5 59-62°, n20D 1.4569, containing 97.2% active O; after 1 mo at room temperature the active O had dropped to 32% and a lower aqueous layer had separated; the organic layer (21 g.) distilled gave 5.1 g. XV, 7.5 g. cyclohexanone, and 3.5 g. yellow liquid, b0.01 68-70°, apparently a condensation product of cyclohexanone with 2 mol Me2CHCH:NH. VI (177 g.) added dropwise with stirring and cooling to 100 cc. H2O, 1 l. MeOH, and 60 cc. H2SO4, warmed, stirred 20 h. at room temperature, poured into 1 l. H2O,

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extd. with Et2O, and the ext. distd. gave 98.8 g. BzH, b16 75°, and left 1.2 g. PhCH:N(O)R (XVI), m. 75°; the original aq. acidic layer treated with 150 g. NaOH in 300 cc. H2O and extd. 3 days with Et2O yielded 73 g. RNHOH (XVII), m. 64-5° (petr. ether), oxidized in air to RNO. III (233 g.) stirred 3 days at room temp. with H2SO4 in aq. MeOH gave similarly 86 g. BzH and 120 g. (crude) R'NHOH (XVIII), b0.02 50-3°, m. 40-2° (sublimed), oxidized by air to R'NO. XVII (4.5 g.) and 5.3 g. BzH heated at 45°, kept 1 h. at 50-60°, and the product isolated with 50 cc. CH2Cl2 gave 5.5 g. XVI, m. 75-6° (petr. ether). VI (8.8 g.) in 100 cc. dry MeCN refluxed 3 days and the resulting nitrone hydrolyzed in the usual manner gave essentially 100% BzH and XVII. XVIII (14.5 g.) and 10.6 g. BzH heated 0.5 h. on the steam bath and the product isolated with 50 cc. CH2Cl2 gave 15.8 g. PhCH:N(O)R' (XIX), m. 103-4°, hydrolyzed with H2SO4 in aq. MeOH to 100% BzH and XVIII. XVII (8.9 g.) and 4.2 g. 30% aq. (CHO)2 shaken 15 min. at room temp. and the product isolated with 100 cc. CH2Cl2 gave 4.7 g. (crude) (RCN(O):CH)2, cream-colored, m. 193-5° (ligroine). p-O2NC6H4CHO (9.1 g.), 8.9 g. XVII, and 100 cc. C6H6 refluxed 10 h. under an H2O-separator gave 10.0 g. p-O2NC6H4CH:N(O)R, yellow, m. 134-5° (3:1 Et2O-petr. ether). XVIII (14.5 g.), 15.1 g. p-O2NC6H4CHO, and 125 cc. C6H6 refluxed 20 h. under an H2O-separator yielded 12.8 g. p-O2NC6H4CH:N(O)R', m. 119-21° (petr. ether). I refluxed 14 h. in 25 cc. PhMe, evapd., and chromatographed on silica gel gave a mixt. of p-O2NC6H4CHO, an unknown material, and 2.7 g. p-O2NC6H4CH:N(O)CHMe2, m. 98-100° (petr. ether). VI (17.7 g.) in 50 cc. Et2O reduced with 3.8 g. LiAlH4 in 200 cc. Et2O gave 14.6 g. V, b0.1 48°. VI (8.9 g.) added dropwise with stirring to 25 g. KI, 100 cc. H2O, 200 cc. EtOH, and 40 cc. AcOH, treated less than 15 min. with NaHSO3, basified, and extd. with Et2O gave 6.5 g. V. XVI (5.6 g.) in 50 cc. Et2O reduced with 1.2 g. LiAlH4 in 200 cc. Et2O yielded 4.3 g. PhCH2NROH, m. 71-3° (ligroine). XIX (7.5 g.) in 50 cc. Et2O reduced with 1.2 g. LiAlH4 in 200 cc. Et2O and decompd. with HCl gave 4.5 g. PhCH2NR'OH (XX).HCl, m. 172-4° (EtOAc). XX.HCl and NaOH in aq. MeOH gave XX, noncrystallizable oil. VII (15.7 g.) in 50 cc. Et2O reduced with 3.8 g. LiAlH4 in 150 cc. Et2O gave 10.4 g. R'NHMe, b19 56-8°, n20D 1.4305; HCl salt, m. 158-9° (EtOAc). R'N:CH2 reduced with LiAlH4 gave 74% R'NHMe. XI (27.6 g.) and 30.4 g. brucine in 80 cc. CH2Cl2 refluxed 16 h. and filtered gave 28.5 g. brucine N-oxide, m. 194° (decompn.); the filtrate washed, dried, and distd. gave 8.1 g. (crude) XI which fractionated yielded 4.3 g. XI, b8.0 60°, n20D 1.4260, α24D -2.80° (neat). VI (35.4 g.) in 100 cc. dry C6H6 treated dropwise with stirring and cooling with 28.4 g. Et2O.BF3 in 50 cc. C6H6, kept 1.5 h. at room temp., and filtered yielded 40 g. BF3 salt of the unstable isomer (presumably cis) of XVI, m. 80-8° (CH2Cl2 at -80°), converted on recrystn. from hot EtOAc to the stable isomer (presumably trans) of XVI, m. 135-7°. XVI and Et2O.BF3 in Et2O at room temp. gave an essentially quant. yield of trans-XVI. At room temp. cis-XVI underwent isomerization to trans-XVI. 2-Butyloxazirane (1.0 g.) and 5.0 g. 2,4-(O2N)2C6H3NHNH2 in 25 cc. concd. H2SO4, 36 cc. H2O, and 125 cc. EtOH kept overnight gave 4.2 g. mixed 2,4-dinitrophenylhydrazones of CH2O and PrCHO; the aq. filtrate basified and distd., the aq. alc. distillate shaken 1 h. at room temp. with 1.35 g. PhNCS, and the product isolated with CH2Cl2 yielded 1.2 g. PhNHCSNH2, m. 152-4°. IX (1.4 g.) gave similarly 4.6 g. mixed 2,4-dinitrophenylhydrazones of equal amts. of PrCHO and iso-PrCHO, and 64% PhNHCSNH2. IV (1.0 g.) under the same conditions yielded 4.0 g. 2,4-dinitrophenylhydrazones of equimolar amts. of CH2O and Me2CO, and 60% MeNH2 (isolated as 1.0 g. PhNHCSNHMe, m. 111-12°). X (1.9 g.) gave similarly 4.6 g. mixed 2,4-dinitrophenylhydrazones of equal amts. of AcH

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and iso-PrCHO; the alk. filtrate steam-distd. gave 0.8 g. PhNH2 (tribromide, m. 120°). X (19.1 g.) added dropwise with cooling and stirring to 8.6 g. KOH in 100 cc. (CH2OH)2, kept 1 h. at 0°, allowed to warm spontaneously to 45°, and heated 1 h. at 60°/5.0 mm. gave 4.1 g. iso-PrCHO (2,4-dinitrophenylhydrazone, m. 179-81°); the mixt. poured into 300 cc. H2O, extd. with CH2Cl2, and the ext. worked up yielded 1.5 g. BzCH:CHCHMe2, m. 139-40°; the mother liquor yielded 3.1 g. PhAc, b12.0 83-5°. VI (5.3 g.) added at room temp. with stirring under N to 12.0 g. Fe(NH4)(SO4)2.6H2O (XXI) in 100 cc. H2O and the product isolated after 2 h. with CH2Cl2 gave 5.2 g. BzNHR, m. 134°. A similar run with only 1.2 g. XXI gave 5.3 g. (crude) BzNHR; the petr. ether washings from the crude product gave 1.5 g. unchanged VI. VII (4.7 g.) and 1.2 g. XXI gave similarly 4.1 g. HCONHR', b0.5 84°, n20D 1.4555. XII (12.9 g.) added with stirring to 8.0 g. XXI in 100 cc. H2O under He while passing the effluent gases through Drierite, Dry Ice-Me2CO, and liq. N traps, the mixt. stirred 36 h. at room temp., extd. 3 days with CH2Cl2, and the ext. distd. gave 4.3 g. Et2CO, b. 96-8°, and 3.2 g. EtCONHEt, b0.5 65°, n20D 1.4369; the cold traps contained C4H10 and 3:1 C2H6-C2H4; the aq. soln. from a duplicate run washed with Et2O, basified, and distd. gave 0.055 mol NH3. XIV (15.7 g.) and 16 g. XXI in 150 cc. H2O stirred 40 h. under N at room temp. gave C4H10 and 2:1 C2H6-C2H4, a trace of PhAc, b12.0 85°, and 11.2 g. EtCONHCHMePh, b0.05 121°, n20D 1.5262, m. 58-60°; the yield of NH3 was 2%. XIII (14.3 g.) and 8.0 g. XXI in 100 cc. H2O stirred 8 h. under He gave 1:1 C3H8-C3H6 and 8.5 g. iso-BuNHOCH, b0.1 60°, n20D 1.4388. VIII (14.3 g.), 16 g. XXI, and 150 cc. H2O stirred 16 h. under He gave 3:1 C3H8-C3H6 and 8.4 g. HCONHR, b0.2 48°, n20D 1.4326. VI (34.4 g.) added dropwise during 2 h. at 200° to a vertical glass tube packed with glass helixes and entrained with 50 cc. N/min. and the effluent gases passed through an ice and Dry Ice-Me2CO trap gave 7.2 g. Me2C:CH2 contaminated with traces of NO, CO2, and RNO; the ice trap contained 27 g. viscous liq. which yielded 8.8 g. PhCH:NOH and 4.1 g. XVI. VII (30.0 g.) pyrolyzed during 2 h. at 200° gave 19.7 g. HCONHR', b0.5 82°, n20D 1.4552. VII (15 g.) in 50 cc. HCONMe2 refluxed overnight, poured into H2O, and extd. with CH2Cl2 gave 11.2 g. HCONHR'. XV (20.0 g.) pyrolyzed during 1 h. at 300° yielded a trace of cyclohexanone and 16.5 g. N-isobutylcaprolactam, b0.7 75°, n20D 1.4750. VIII (25.3 g.) pyrolyzed during 2 h. at 250° gave 15.9 g. iso-PrCONHR, m. 118-20° (also obtained from iso-PrCOCl and RNH2), and 3.2 g. unchanged VIII. XIII (20.0 g.) pyrolyzed at 300° gave 9.7 g. iso-Bu-(iso-Pr)NOCH (XXII), b3.0 78-80°, n20D 1.4409, and 4.9 g. iso-PrCONHCH2CHMe2 (XXIII), m. 43-5°, b0.2 85-8°. iso-BuNHCHMe2 (8.0 g.) treated with stirring with 10.5 g. CCl3CHO and kept at room temp. overnight yielded 7.5 g. XXIII, b1.0 65°, n20D 1.4411. Iso-PrCOCl (11.2 g.) in 100 cc. dry Et2O treated with stirring with 14.6 g. iso-BuNH2, refluxed 1 h., and worked up gave 13.0 g. XXIII, m. 43-5°, b0.1 82°. XI (100 g.) pyrolyzed during 4 h. at 300° yielded 67.0 g. mixt. of 64% iso-BuCONMePr (b5.0 93°, n20D 1.4437, from iso-BuCOCl and MeNHPr) and 36% iso-BuPrNAc (b5.0 91°, n20D 1.4440, from iso-BuNHPr and Ac2O). XI (25.0 g.) pyrolyzed at 300° yielded 13.9 g. mixt. of 39% iso-PrPrNAc (b5.0 68-70°, n20D 1.4437, from iso-PrNHPr and Ac2O) and 61% iso-PrCONMePr (b5.5 67°, n20D 1.4409, from iso-PrCOCl and MeNHPr). XI (27.6 g.) refluxed 2 h. under N at 168 to 128° and the effluent gases passed over aq. H3BO3 showed the formation of 0.057 mol NH3; the liq. product distd. gave 16.1 g. iso-BuAc, b. 114-16°, 0.8 g. unreacted XI, and 1.0 g. mixed amides, b3.0 68-70°. XIII (25.0 g.) refluxed 3 h. under N at 165 to 105° yielded 8.0 g.

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iso-PrCH:NCH2CHMe2, b47 60°.

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AB Hydrogenation to unsatd. and saturated alcs. and glycols, hydration, addition of HCl and NaHSO3, oxidation of VIa to (HOCR3R4C.tplbond.C)2 (XXIIIc), esterification and etherification, and the preparation of amino- and haloalkynes are discussed. A selective catalyst (XXIV) for hydrogenation of VIa to olefinic alcs. is prepared by vacuum impregnating 1 kg. granular kieselguhr with solns. of 0.65 g. PdCl2 and of 13 g. FeCl3 each in 400 ml. H2O, drying, boiling 1 l. 0.5 hr. with 500 ml. concentrated water glass solution and 2.5 l. H2O, filtering (vacuum) after 12 hrs., drying at 100°, and reducing with H at 140-50°. XXIV contains 1.5% free alkali. Distillation of 500 g. condensate from passing 25% aqueous XX and H over XXIV at 140-50° gives a little EtCHO, a mixture (b. 80-92°) containing 110 g. CH2:CHCH2OH, 12 g. PrOH with 12% H2O, and a trace of XX. Similarly prepared from the corresponding VIa are: CH2:CHCH(OH)Me, b. 97° (azeotrope containing 26% H2O, b. 85-6°); Me2C(OH)CH:CH2, b. 99°; CH2:CHCMe(OH)Et, b. 118°; and 1-vinyl-1-cyclohexanol, b2077°, m. 4°. These compds. can also be prepared with Fe powder (prepared from Fe carbonyl) as catalyst at 50°, 100 atmospheric H, reduction being stopped when the calculated amount of H has reacted. XXIII (200 g.), hydrogenated at room temperature and 50 atmospheric over 5 g. Raney Ni until half the calculated amount of H has reacted, then at 80° and 200 atmospheric to complete reaction gives 185 g. Me2C(OH)Et, b. 102°. PrOH, sec-BuOH, MeEt2COH, b. 124°, and 1-ethyl-1-cyclohexanol, b40 93°, are prepared similarly. Catalyst for preparing aldehydes and ketones from acetylenic alcs. is prepared from 500 g. kieselguhr containing 3% Fe, and 0.6% S (as SO4--), made into a paste with 5 g. PdCl2.2H2O in 200 ml. H2O, dried, powdered, pelleted, and reduced with H at 200°. XX (35 g.) and 15 g. H2O are vaporized over 100 ml. of this catalyst at 105° and 40 l. H for 1 hr. Distillation of 500 g. of condensate gives 300 g. EtCHO. MeCOEt is prepared similarly from XIb. Crude IX from 30% VIII, 1.5 kg., hydrogenated over 50 g. Raney Ni (or other common hydrogenation catalysts) at 40-60° and 200 atmospheric (with cooling to control reaction) gives 500 g. (CH2CH2OH)2, m. 20.1°, b. 229, b0.7 106°, d20 1.069, nD20 1.4461, bis-urethan, m. 198-200°. HOCH2CH2CH2CH(OH)Me, b15 125-8°, [MeCH(OH)CH2]2, b18 132-3°, b0.4 95-1000 (diacetate, b15 114°), [Me2C(OH)CH2]2, b15 117-18°, m. 91° (from EtOAc), and 1,1'-ethylenedicyclohexanol, b2 145°, m. 128-30°, are also prepared in similar yields. (CH2CH2OH)2 (180 g.) heated 4 hrs. with 5 g. FeCl3 and 60 g. (CH2O)n (or 30-40% VIII) gives 184 g. acetal, b. 117°. IX (500 g. 33%), and 50 g. Fe (prepared from Fe carbonyl), treated at 50° with 100 atmospheric H and reaction stopped when the calculated amount of H has reacted give 150 g. (HOCH2CH:)2 (XXV), b. 237-9°, b3 116-21°, m. 4°; diacetate, b13 108-10°; " formaldehyde acetal," b. 126°. Other suitable catalysts are Co, poisoned by adding 0.1% KSCN to the solution, and 0.2% Pt-C treated with 0.15% Na2HPO4, 0.1% H3BO4, or 1.5% C5H5N. Partial hydrogenation is also obtained with H containing 3-5% CO. [MeCH(OH)CH:]2, b6 109-11°, [Me2C(OH)CH:]2, b20 120-2°, m. 77°, and 1,1'-vinylenedicyclohexanol, m. 154°, are prepared similarly in nearly quant. yield. XX hydrated by heating 1500 g. 30% aqueous solution with 50 g. HgSO4 and 5 g. concentrated H2SO4 to 70° until the carbonyl number is constant, the mixture neutralized, the H2O azeotroped off with CH2Cl2 or XIIa,

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and the residue distd. give 350 g. HOCH2Ac, b15 49-51°. The following compds. are similarly hydrated (amt. of starting compd., and the product, and its yield and b.p. given): MeOCH2C.tplbond.CH, 105 g., MeOCH2Ac, 100 g., b. 114-16°; XIb, -, MeCH(OH)Ac, no yield, b. 138-40°; (MeOCH2C.tplbond.)2 (XXVa), -, MeOCH2COCH2CH2CH2OMe, -, b17 83-5°; IX, 172 g., HOCH2COCH2CH2OH (XXVI), 120 g., b0.6 108-10° [also prepd. in 65% yield from 500 ml. 10% aq. HOCH2COCH:CH2 (XXVII) and 6 g. concd. H2SO4, 20-30 hrs. at 30°]; and [MeCH(OH)C.tplbond.]2, -, MeCH(OH)COCH2CH(OH)Me, -, b2 96-8°. XXIIIa (700 g.) refluxed 3 hrs. with 40% H2SO4 gives 280 g. 1-acetyl-1-cyclohexene, b10 73-5°. HgO (5 g.), 2 g. BF3-Et2O, and 2 g. MeOH warmed to 60-70°, mixed with 64 g. MeOH, and 56 g. XX added with stirring at 50-60° so that the mixt. refluxes smoothly, cooled after a sample no longer gives a ppt. with ammoniacal XI give 55 g. 2,5-dimethyl-2,5-dimethoxy-1,4-dioxane, m. 126-8° (from MeOH); the 2,5-di-EtO analog, prepd. analogously, m. 73-4°. Aq. XX (25%) passed at 330° (80 ml./hr.) through a 1-m. long porcelain tube contg. 450 ml. catalyst (20% Cu, 1-2% Cr2O3 on silica gel, activated with H at 200-50°) gives 63% CH2:CHCHO. H2C:CHAc, prepd. in 50% yield from XIb at 280-300° over 6% H3PO4 and 50% NaH2PO4 on graphite, b130 33°. XXVI, b10 45°, is prepd. in 20-g. yield (90% pure) from 5 g. HgO, 1.5 g. Cl3CCO2H, 5 g. BF3-Et2O, and 5 g. EtOAc heated to 50-60°, cooled, added to 100 g. IX in 400 g. EtOAc, warmed to 40°, evacuated until the mixt. refluxes at 45°, and the mixt. neutralized with Na2CO3 and distd. when the temp. drops rapidly (about 1 hr.). This compd. polymerizes in light to a gel and, finally, to a solid, transparent, odorless, high-mol.-wt. product. XXVI (300 g.) added to 700 g. boiling Ac2O, and refluxed 1 hr., gives 260 g. AcOCH2COCH:CH2, b12 81°, polymerizes to a gummy mass in a few days; 256 g. heated to 60° with 0.5 g. p-PhCH2NHC6H4OH 2 days gives 240 g. 2-acetoxyacetyl-6-acetoxymethyl-2,3-dihydropyran, b1 171°, m. 49°. IX (430 g.) in 700 ml. MeOH, added to catalyst mixt. prepd. by warming 15 g. HgO, 15 g. BF3Et2O, and 30 ml. MeOH, the temp. held to 30° by cooling, warmed a short time with 500 ml. 1% H2SO4 after reaction heat has died away, neutralized with Na2CO3, filtered, and distd. gives MeOCH2CH2COCH2OH (XXVIII), b7 84-7°. Sepg. Hg from the soln., distg. the excess MeOH, and cooling the mixt. gives 2,5-dimethoxy-2,5-bis(β-methoxyethyl)-1,4-dioxane, m. 82°; this hydrolyzes to XXVIII on warming with dil. H2SO4. EtOCH2CH2COCH2OH, b16 104-6°, and iso-PrCH2CH2COCH2OH, b5 94°, are prepd. analogously. H2SO4 (35 g.) and 125 g. 50% HOCH2C.tplbond.CCHMeOH treated at 60° and 130 mm. with an addnl. 375 g. of the diol gives 60 g. CH2:CHCOCH2CH2OH (or MeCH:CHCOCH2OH), b18 75°. [MeCH(OH)C.tplbond.]2 (200 g.) in 800 ml. H2O mixed with 10 g. HgSO4 in 60 g. 17% H2SO4 at 30-5° (with cooling) gives 140 g. MeCH:CHCOCHMeOH, b2 48°. Hydrogenation of the corresponding oxo alcs. or glycols over Raney Ni at 200 atm. and 25-120° gives the following compds. in good yield: [MeCH(OH)]2 (XXVIIIa), b. 179°; HOCH2CHEtOH, b. 191°, b10 96-7°, from XXVII [40% soln. of XXVI (prepd. from 500 g. 33% aq. IX, 5 g. HgSO4, and 10 g. concd. H2SO4 at 30°) adjusted to pH 5 with CaCO3 and the ppt. filtered off and hydrogenated at 150° and 100 atm. gives 120 g. XXVIIIa; diacetate, b20 85-90°]; HOCH2CH(OH)CH2CH2OH, b1 130-1° (cyclic formaldehyde acetal, C5H10O3, prepd. with (CH2O)n and FeCl3, b. 198-9°, b0.1 67-8°). The following HOCH2CH(OH)CH2CH2OR are similarly prepd. from the 2-oxo precursor (R given): Me, b12 116°; Et, b10 122°; iso-Pr, b10 126-7°; tert-Bu, b4 110-11°. [MeCH(OH)C.tplbond.]2 (400 g.) and 600 ml. H2O stirred and treated at 70-80° during 40 min. with 40 g. HgSO4, neutralized

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after 25 min. with Na2CO3, made weakly acidic with dil. H2SO4, neutralized with CaCO3, filtered off, and hydrogenated at 100° and 200 atm. over 200 g. "nickel-chromium oxide" catalyst, give 150 g. Me[CH(OH)]2Pr, b0.7-0.8 102° (gives deep blue color with CuSO4-NaOH), and a little Me[CH(OH)]2CH2CHMeOH, b0.7 140-50°. HOCH2CHEtOH (50 g.) and 5 g. p-MeC6H4SO3H (or KHSO4) heated rapidly to 160° with removal of H2O give 4 g. PrCHO and 25 g. 2,5-diethyldioxane, b21 62°; 50 g. XXVIIIa and 6 g. of a mixt. of equal parts of p-MeC6H4SO3H and KHSO4 give 65 g. 2,3,5,6-tetramethyl-1,4-dioxane, b. 138-9°; HOCH2CH(OH)CH2CH2OH gives 0% 2,5-bis(β-hydroxyethyl)dioxane, b20 90°. XIb (125 g., 60%) is added during 5 hrs. to 500 ml. of a distg. soln. contg. 3.8% FeSO4, 41.4% Fe2(SO4)3, 0.15% HgSO4, and 1.2% H2SO4 (the original vol. maintained by adding H2O) and the distillate satd. with NaCl and redistd. gives 20 g. Ac2, b. 87-8°. (MeCH(OH)C.tplbond.)2 (300 g.) refluxed with 143 g. 80% H3PO4, 1.5 g. HgSO4, and 1 l. H2O, gives 260 g. AcCOPr, b150 82-5°, dioxime, m. 173°, dioxime-nickel complex, orange-red, m. 158-60°, and as by-product, 2,5-dimethyl-3-oxotetrahydrofuran, b150 94-5° (semicarbazone, m. 168-71°). HOCH2CH(OH)Et passed at 180° over granular CuO is converted in 32% yield to a mixt. contg. about 45% EtCOCHO (XXIX) and HOCH2COEt. IX (200 g.), 40 g. HgCl2, and 400 g. (CH2OH)2 heated 4 hrs. at 185° give 160 g. XXIX diethylene glycol acetal (C8H14O4), b12 100-5°, which partly crystd. on standing; 100 g. of this and 500 ml. 1% H2SO4 stirred 9 hrs. at 90° give XXIX, which polymerizes rapidly (dioxime, m. 129°), and XXIX monoethylene glycol acetal, b12 90-5°. XXVI (104 g.) and 300 ml. 30% VIII added at 70-80° to 500 g. CuSO4 in 2 l. H2O and 2 kg. 20% NH3, held at 70-85° 1-2 hrs., and the Cu complex filtered off, suspended in H2O, decompd. with H2S, and the aq. soln. distd. give (2-hydroxyethyl)imidazole, b1 170-5° (picrate, m. 144°); this with SOCl2 gives (β-chloroethyl)imidazole which with alc. NH3 gives histamine di-HCl, m. 236-8° (picrate, m. 144°). IX (60 g.) heated 13 hrs. with 150 g. MeOH and 3 g. ZnCO3, gives EtCH(OH)CO2Me, b30 68°; other esters of this acid prepd. similarly are: Et, b. 167-9°; Bu, b. 200-2°; allyl, b20 85-8°; PhCH2, b33 170-5°; and cyclohexyl, b37 145-50°. HCl passed into 112 g. XX and 6 g. HgCl2 heated to 60°, the soln. neutralized with alkali when the temp. falls to 70° after reaction ceases, and satd. with K2CO3 gives 140 g. CH2:CClCH2OH, b. 135-40°; also prepd. (225 g.) from 500 g. 30% aq. XX, provided HCl addn. is rapid and temp. held to 80°. XX (60 g.), 100 g. NaHSO3, and 100 ml. H2O refluxed several hrs., cooled, filtered, and dild. with MeOH gives NaO3SCH2CH(SO3Na)CH2OH; analogously, XXIII gives NaO3SCH2CH(SO3Na)CMe2OH and 200 g. IX give 260 g. HOCH2(CHSO3Na)2CH2OH. Aq. XX (30 ml. 27.16%), 85 ml. H2O, 9 g. XI, and 25 g. NH4Cl shaken with O at 0° give 9.6 g. (HOCH2C.tplbond.C)2, m. 111-12° (from Et2O-petr. ether) (also prepd. in quant. yield by a continuous process), which hydrogenates in MeOH over Raney Ni at 60° and 200 atm. to give 1,6-hexanediol, m. 41.5°, b13 143°. Other RC.tplbond.CH oxidized similarly in quant. yield to (RC.tplbond.C)2 are (R and product consts.): MeCHOH, m. 69-90° (mixt. of stereoisomers, m. 68° and 109°, resp.); CH2:CH, b3 40°; and HO2CCH2CH2, decomp. above 220°. A mixt. of 60 g. H2C:CHC.tplbond.CH and 70 g. XXIII gives HOCMe2C.tplbond.CC.tplbond.CCH:CH2, b3 75°. XX (9 ml. 97.5%) added to 35 g. Cu(OAc)2.H2O and 30 g. NH4Cl in 90 ml. H2O (boiled in N) pptd. greenish yellow C3H3OCu2Cl. The following esters of XX are prepd. by conventional methods: acetate, b. 110-12°; carbonate (C7H6O3) (from COCl2), b20 97°; adipate (C12H14O4), b4 142-5°; benzoate, b9 102-7°; p-nitrobenzoate, m.

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88-90° (from ligroine); benzenesulfonate (XXX), b2 140-2°; and p-toluenesulfonate (XXXI), b5 161-2°. Also prepd. is HC.tplbond.CCH(OAc)Et, b. 139-40°. XIb esters prepd. are: acetate, b. 124-6°; benzoate, m. 27-9° (from ligroine); and p-toluenesulfonate, m. 58-60° (from cyclohexane). Also prepd. is (AcOCH2C.tplbond.)2, b3 106°. Me2SO4 (75 g.) added at 40° to 56 g. XX in 44 ml. H2O and 110 g. 50% NaOH so that the temp. stays below 60°, stirred 2 hrs. at 50-60°, and distd. gives 62 g. MeOCH2C.tplbond.CH, b. 65°. Ethylene oxide (45 g.) and 58 g. 96% XX added rapidly and simultaneously to 300 ml. 2% NaOH and neutralized after 1 hr. give 41 g. HOCH2(CH2OCH2)2C.tplbond.CH, b12 76-7°, b14.5 79-80°. CH2:CHCN (53 g.) added to 60 g. 94% XX (dried over K2CO3 just before use) and 0.5 g. powd. NaOH, the temp. allowed to rise to 100°, then held at 50° 1 hr. with cooling, neutralized with dil. H2SO4 and distd. gives 75 g. HC.tplbond.CCH2OCH2CH2CN, b13 101-2°. PhOH (200 g.), 500 g. XXX, 315 ml. 35% NaOH, and 1.5 l. H2O stirred 2 hrs., heated to 90-5°, poured onto ice, and extd. with Et2O give 200 g. HC.tplbond.CCH2OPh, b10 81-3°. Other HC.tplbond.CCH2OR prepd. similarly using XXX or XXXI are (R and m.p. or b.p.): o-O2NC6H4, m. 78-9° (from MeOH); p-O2NC6H4, m. 118-20°; o-OCHC6H4, m. 72-4° (from ligroine); pyrocatechol, b13 121-4°; β-naphthyl, m. 64-6° (from MeOH). Crude XXX (670 g.), and 250 ml. 35% NaOH added in 4 portions to 250 g. o-HOC6H4NHAc in 1670 ml. H2O, the mixt. heated 1 hr. to 90°, treated with 30 ml. NaOH, cooled, and extd. with Et2O, the ext. washed with 15% HCl, then 5% NaOH, and evapd., and the residue heated 1 hr. with 1 l. 1:1 HCl give 81 g. o-HC.tplbond.CCH2OC6H4NH2. Similarly, p-HOC6H4CO2Me gives p-HC.tplbond.CCH2OC6H4CO2H, m. 212-14° (from MeOH) 40 g. XXX gave 10 g. p-HC.tplbond.CCH2OC6H4NHAc, m. 109-11°; hydrolysis gives the amine, b4 118-20°, from which an azo dye is prepd. by diazotization and coupling with 1-phenyl-3-methyl-5-pyrazolone. (XXVa) b14 58°, is prepd. in 400 g. yield by adding 1350 g. Me2SO4 and 1075 g. 40% NaOH to 400 g. IX in 400 ml. H2O at 40° so that the temp. remains const. without heating, stirring 2 hrs. at 50-60°, sepg. layers, treating the lower layer with another 600 g. Me2SO4 and 475 g. 40% KOH, and distg. the org. layers. Similarly 72 g. XXIII gives 65 g. (Me2C(OMe)C.tplbond.)2 (XXXII), b19 86-8°. Heating 172 g. 50% IX and 400 g. 50% NaOH to 80°, adding 250 g. MeHSO4 during 1 hr., stirring 4 hrs., and extg. with Et2O, gives 26 g. HOCH2C.tplbond.CCH2OMe, b30 106°, and 24 g. XXVa. Freshly distd. PhNH2 (93 g.) and 196 g. XXX mixed in an ice bath (temp. rises to 120°), the soln. cooled, 100 ml. Me2CO added, the crystals washed with Me2CO, the combined filtrate and washings steam distd., the distillate extd. with Et2O, the ext. dried and distd., the base (b28 146-52°) (37 g.) dild. with 50 ml. C6H6, refluxed 1 hr. with 25 ml. Ac2O, and extd. with HCl, and the ext. neutralized give 11 g. PhN(CH2C.tplbond.CH)2, b4 94-6°. PhNR1R2 prepd. similarly, using XXXI or the benzene-sulfonate of XIb, are (R1 and R2 given): Me, CH2C.tplbond.CH, b4 80-3°, m. 35-6°; Me, CHMeC.tplbond.CH, b1 76-8°; CH2CH2OH, CH2C.tplbond.CH, b2 135-7°; and CH2CH2OH, CHMeC.tplbond.CH, b3 137-40°. IX (344 g.) treated during 10 min. with 1200 g. SOCl2, left overnight at 10-15°, warmed to 80°, SOCl2 removed at the H2O pump, and the residue distd. gives 370 g. (ClCH2C.tplbond.)2 (XXXIII), b16 65-6° (reagents in this prepn. must be freshly distd. and the distn. residue must not be heated above 100° or an explosion may occur). (Me2CClC.tplbond.)2, prepd. similarly, b11 60-70°. IX (344 g.), and 476 g. SOCl2 as above gives a lava-like mass which, crystd. from Ac2O or HCONMe2, gives the cyclic disulfite

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(C8H8O6S2) (XXXIV), colorless crystals, m. 196-7°, of IX; IX is recovered in 8.4-g. yield by heating 25 g. XXXIV 0.5 hr. with 100 ml. 30% NaOH. Adding 57 g. 40% aq. NaOH at 75° to 12.3 g. XXXIII in 50 ml. EtOH gives 1.9 l. (HC.tplbond.C)2. XXXIII (123 g.) treated with 430 g. pyrrolidone 2 hrs. at 20° gives 170 g. 1,1'-(2-butynylene)dipyrrolidine, b2.5 116-16.5°; 1,4-dipiperidino deriv. (70 g. from 62 g. XXXIII and 180 g. piperidine) b5 160-1°.

ACCESSION NUMBER: 1956:89208 CAPLUS
DOCUMENT NUMBER: 50:89208
ORIGINAL REFERENCE NO.: 50:16774b-i,16775a-i,16776a-i,16777a-d
TITLE: Ethynylation. IV. Reactions of α-alkynols and γ-alkynediols
AUTHOR(S): Reppe, Walter; et al.
SOURCE: Ann. (1955), 596, 38-79
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 50:89208

L14 ANSWER 30 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB The following N,N-disubstituted 3-hydroxy-2-pyridylmethylamines are prepared by heating 3-hydroxypyridine and the resp. amine in H2O or EtOH with a 30% formalin solution for 2 hrs. and distilling the product: di-Me (I), b0.3 60°, m. 56-9°; di-Et (II), b2.7-3.7 90-110°; di-Bu (III), b1.3 110-20°; methylbenzyl (IV), b1.3 126-35°. Also 1-(3-hydroxy-2-pyridylmethyl)piperidine (V), b0.8 95-7°. I is converted to the methobromide (VI), m. 175-7°, with MeBr and the di-HCl salt (VII), m. 178-86°, with alc. HCl. The following carbamates are prepared by warming the resp. 3-hydroxy-2-pyridylmethylamine in pyridine or C6H6 with Me2NCOCl, allowing the mixture to stand at room temperature for 16 hrs., removing the solvent, and treating the residue with anhydrous HCl, yielding HCl salts. Dimethylcarbamate of: I.HCl, m. 128-30°; I.2HCl, m. 163-7°; II.2HCl, m. 117-19°; IV.2HCl (VIII), m. 167-9°; V.2HCl, m. 111-25°. With MeBr instead of anhydrous HCl above are obtained the dimethyl carbamates of: I.MeBr, m. 175-7°; III.MeBr, m. 154-5°; V.MeBr, m. 156-7; II.MeBr, m. 141-3°. By substitution of the respective carbamyl chloride for Me2NCOCl, the following di-substituted carbamates of I.MeBr are obtained: (p-bromophenyl)methyl, m. 176-8°; methyl-p-tolyl, m. 153-5°; diiso-Pr, m. 173-5°. Similarly the carbanilate of I, m. 91.5-4.5°, and the N-methylcarbanilate of II.HCl, m. 142-4°, are prepared VIII yields on reduction with H and PdCl2 on charcoal the dimethylcarbamate of 3-hydroxy-N-methyl-2-pyridylmethylamine-2HCl, m. 140-1°. To 15 g. 3-hydroxypyridine and 30 g. PhNHCH2CH2NEt2 in 100 cc. of 70% EtOH is added 13.5 cc. of 35% formaldehyde solution, the mixture refluxed for 2 hrs., the solvent removed, and the residue treated with dilute HCl, yielding N,N-diethyl-N'-phenyl-N'-(3-hydroxy-2-pyridylmethyl)ethylenediamine-HCl (IX), m. 199-200°; the free base can be methylated with CH2NH2 and then treated with dilute HCl, yielding N,N-diethyl-N'-phenyl-N'-(3-methoxy-2-pyridylmethyl) ethylenediamine-2HCl, m. 72-4°. The free base of IX treated with Me2NCOCl and then with MeBr gives the dimethylcarbamate of N,N-diethyl-N-(2-[N'-(3-hydroxy-2-pyridylmethyl)-N'- phenylamino]ethyl)-N-methylammonium bromide, m. 172-3.5°. 3-Hydroxypyridine and Et2NCH2CH2NEtCH2Ph and 35% HCHO solution in 70% EtOH yield N,N-diethyl-N'-benzyl-N'-(3-hydroxy-2-pyridylmethyl) ethylenediamine-2HCl, m. 180-1°.

ACCESSION NUMBER: 1950:46950 CAPLUS
DOCUMENT NUMBER: 44:46950
ORIGINAL REFERENCE NO.: 44:8961h-i,8962a-e
TITLE: Carbamic acid esters of 3-hydroxy-2-pyridylmethylamines
INVENTOR(S): Aeschlimann, John A.; Stempel, Arthur
PATENT ASSIGNEE(S): Hoffmann-La Roche Inc.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2512732		19500627	US	

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AB Iso-PrNH2 (118 g., 2 mol) at 17-20°, treated with 2 mol of 36% aqueous HCHO and then with 2 mol of Me2CHNO2 with stirring for 30 min., 20 g. Na2SO4 added, and the nonaq. layer allowed to stand at room temperature for 5 days and distilled, gives 76% of N-(2-nitroisobutyl)-isopropylamine (I), b10 84°, nD20 1.4339, d2020 0.9685 (all n and d. under these conditions). Iso-PrNH2 (59 g.) and 119 g. Me2C(NO2)CH2OH, shaken and allowed to stand 3 days at room temperature, give 86% of I. Iso-PrNH2 (2 mol) and 2 mol 30% aqueous HCHO, treated during 30 min. with 1 mol of EtNO2, give 71% of 2-nitro-2-methyl-1,3-diisopropylaminopropane (II), b3 98-100°, n 1.4518, d. 0.9671. II results also in 60% yield from 2 mol of iso-PrNH2 and 1 mol of O2NCMe(CH2OH)2 on standing at room temperature for 3 days. The following were similarly prepared by using HCHO and the other reactants named: N-(2-nitroisobutyl)methylamine (MeNH2 and Me2CHNO2), 48%, b6 60-2°, n 1.4368, d. 1.0166; N-(2-nitro-2-methylbutyl) isopropylamine (iso-PrNH2 and 2-nitrobutane), 90%, b10 95-7°, n 1.4409, d. 0.9625; N-(2-nitroisobutyl)butylamine (BuNH2 and Me2CHNO2), 85%, b10 105-7°, n 1.4407, d. 0.9584; N-(2-nitroisobutyl)-1-methylpropylamine (EtMe-CHNH2 and Me2CHNO2), 72%, b10 96°, n 1.4384, d. 0.9571; N-(2-nitroisobutyl) benzylamine (PhCH2NH2 and Me2CHNO2), 75%, b2 130-3°, n 1.5178, d. 1.0785; 2-nitro-2-chloro-1,3-dibenzylaminopropane (PhCH2NH2 and ClCH2NO2), 80%, m. 74.9°; N-(2-nitroisobutyl)-2-phenylethylamine (MePhCHNH2 and Me2CHNO2), b0.8 121-4°, n 1.5080, d. 1.0809; N-(2-nitroisobutyl)-2-amino-2-methyl-1-propanol (Me2C(NH2)CH2OH and Me2CHNO2), 90%, m. 59°; N-(2-nitroisobutyl)-2-amino-1-butanol (EtCH(NH2)CH2OH and Me2CHNO2), 10%, m. 58.1°. The nitro amines (100 g.) in 100 mL. MeOH were reduced over 5 g. Raney Ni at 30-50° and 500 lb./sq. in. H pressure, the MeOH being removed at atmospheric pressure and the H2O by distillation with C6H6; the same yields were obtained with crude or pure nitro amines (on the basis of the nitro paraffins). N-(2-Aminoisobutyl)methylamine, b750 123°, n 1.4293, d. 0.8149; 2-amino 2-methyl-1,3-diisopropylaminopropane, b3 98-100°, n 1.4502, d. 0.8596; N-(2-aminoisobutyl) isopropylamine, b760 147.3°, n 1.4263, d. 0.8025; 2-amino-2-ethyl-1,3-diisopropylaminopropane, b1 71-2°, n 1.4491, d. 0.8520; N-(2-aminoisobutyl)butylamine, b10 64-6°, n 1.4346, d. 0.8154; N-(2-aminoisobutyl)-1-methylpropylamine, b10 56-8°, n 1.4297, d. 0.8171; N-(2-amino-2-methylbutyl) isopropylamine, b10 57.5°, n 1.4348, d. 0.8166; N-(2-aminoisobutyl)benzylamine, b8 105-6°, n 1.5153, d. 0.9526; N-(2-aminoisobutyl)-1-phenylethylamine, b5 110°, d. 0.9373; N-(2-aminoisobutyl)-2-amino-2-methylpropanol, b10 115-16°, n 1.4651, d. 0.9360; N-(2-aminoisobutyl)-2-aminobutanol, b10 118-21°, n 1.4631, d. 0.9343.

ACCESSION NUMBER: 1946:8259 CAPLUS
DOCUMENT NUMBER: 40:8259
ORIGINAL REFERENCE NO.: 40:1444a-h
TITLE: Reaction of primary aliphatic amines with formaldehyde and nitro paraffins
AUTHOR(S): Senkus, Murray
CORPORATE SOURCE: Commercial Solvents Corp., Terre Haute, IN
SOURCE: Journal of the American Chemical Society (1946), 68, 10-12
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal

L14 ANSWER 31 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 40:8259

L14 ANSWER 32 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
AB To gain an insight into the course of the reaction of phenols and amines or amides with HCHO, as well as the hardening of such mixed condensates, model expts. have been carried out. 2,4,6-Me2(HOCH2)C6H2OH (I) (3 g.), 5.4 g. NH2CO2Et and 10 g. K2S2O8, heated at 55° for 18 hrs., give N-(2-hydroxy-3,5-dimethylbenzyl)ethylurethan (II), m. 67°. Attempts to condense I with AcNH2 or BzNH2 failed in acid or alkaline solution because the hydrolysis of the amide was more rapid than the condensation. With K2S2O8 at 65°, I and AcNH2 give CH2(NHAc)2 and CH2(C6H2Me2OH-3,5,2) (III); likewise, BzNH2 yielded CH2(NHBZ)2 and III; the intermediate in this reaction is assumed to be the ether (IV), [Me2(OH)C6H2CH2]2O. I is unchanged on heating at 65° for 18 hrs. but with K2S2O8 it gives a good yield of III; IV is unchanged on heating at 105° for 10 hrs. but with K2S2O8 it also gives III. The condensation product of I and CO(NH2)2 [2,4,6-Me2(HZNCONHCH2)C6H2OH] (V) (3.5 g.), 3 ml. 40% HCHO and 200 ml. saturated Ba(OH)2, allowed to stand overnight, give N1-methylol-N2-(2-hydroxy-3,5-dimethylbenzyl)urea, Me2(OH)C6H2CH2NHCONHCH2OH, m. 162°. V (4 g.) in 200 ml. 50% MeOH, 5 ml. 40% HCHO and 15 ml. 2 N NaOH, allowed to stand overnight, yield N1,N1-methylenebis(N2-2-hydroxy-3,5-dimethylbenzylurea) (VI), CH2(NHCONHCH2C6H2Me2OH)2. m. about 200° (decomposition). Distn. of V at 12 mm. gives 6,8-dimethyl-3,4-dihydrocoumaraz-2-one (VII), m. 182.5°; it also results by heating II at 300° or from the N-Me derivative of V at 12 mm. It is believed that the formation of VII does not play a role in the hardening of resins. Although the lactone bridge in VII is not cleaved by concentrated H2SO4 in EtOH, 2 N NaOH gives a mol. compound, m. 101-15° (decomposition), of Me2(HO2CNHCH2)C6H2OH and 2-hydroxy-3,5-dimethylbenzylamine (VIII); this was cleaved by boiling with C5H5N and VIII was purified through the HCl salt (m. p. of VIII not given).
ACCESSION NUMBER: 1944:18455 CAPLUS
DOCUMENT NUMBER: 38:18455
ORIGINAL REFERENCE NO.: 38:2648f-i,2649a
TITLE: Phenol-urea condensation products and the formation of coumarazones
AUTHOR(S): Nystrom, Holger
SOURCE: Kunststoff-Tech. u. Kunststoff-Anwend. (1942), 12, 81-4
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Cyclohexanone (50 g.), 95 g. PhNH2, 88 cc. concentrated HCl and 13 cc. EtOH, warmed 4 days on the H2O bath, give 53 g. PhNH2, 1.5 g. cyclohexenylaniline (I) and 70 g. di-aminodiphenylcyclohexane (II); if the condensation is continued for 12 days, there result 35 g. PhNH2, 2.3 g I and 99 g. II. I pale yellow, b14 175°; HCl salt, m. 228°; Picrate, m. 170°; Ac compound, m. 152°; Bz compound, m. 177°; phenylthiourea. m. 144°; benzal compound, m. 82°. Reduction gives p-cyclohexylaniline, m. 45°; warming I with PhNH2 in HCl or better with PhNH2.HCl gives II. II, b0.1 248°, m. 114°; HCl salt, m. 235°; Ac compound, m. 266°; diphenylthiourea, m. 163°. Warming 114 g. II, 78 cc. concentrated HCl and H cc. EtOH 12 days at 100° gives 5 g. PhNH2, 8 g. I and 96 g. II. A slight decomposition of II takes place upon heating at 305°; a little HCl, H2SO4, HBr or ZnCl2 causes a more marked decompm.; H3PO4 or Cl3CCO2H has no action. PhNHMe (107 g.) and cyclohexanone (50 g.), heated 12 days as above, give 123 g. 1,1-di[methyl-amino]diphenylcyclohexane, b0.3 250-2°, m. 124° (HCl salt. m. 220°; picrate, m. 105°; di-Ac derivative, m. 185°; diphenylthiourea, m. 166°) and 3.5 g. N-methylcyclohexenylaniline, b14 184° (HCl salt, m. 212°; picrate, m. 114°; Ac derivative, m. 85°; N-NO compound, m. 80°). PhNMe2 (123 g.) and 50 g. cyclohexanone give 125 g, di[dimethylamino]diphenylcyclohexane, b12 282-3°, m. 164° (HCl salt, m. 180°; picrate, m. 148°; dimethiodide, m. 178°) and 4.5 g. cyclohexenyldimethylaniline (III). b14 190°, m. 56° (HCl salt, m. 195°; picrate, m. 162°; methiodide, m. 190°). 1,1-Amino[dimethylamino]diphenylcyclohexane, light yellow, b0.3 250-5°, m. 101° (HCl salt, m. 115°); distillation with a couple drops of dilute HCl gives PhNMe2 and I. 1,1-Dimethylaminophenyl[diethylaminophenyl]cyclohexane, b0.1 260-5°, m. 108° (HCl salt, m. 141-2°, strongly hygroscopic). Condensation with α-C10H7NH2 is slow, the yield being only 13% after 90 hrs.; the compound, C24H23N2, b0.1 270-80°, m. 152°. III in fuming HBr gives the Compound C14H20NBr, m. 95° (20% yield) (picrate, m. 152°). Cyclohexanone (20 g.) and 50 g. tetrahydroquinoline give 5 g. 6-cyclohexenyltetrahydroquinoline, b0.1 163-5°(HCl salt, m. 120°; picrate, m. 90°) and 30 g. 1,1-di[tetrahydroquinolyl]cyclohexane, b0.1 265-7° m. 114° (di-NO compound, m. 85°; di-Bz derivative, m. 154°; diphenylthiourea, m. 92°). m-MeC6H4NH2 gives only a few % of 3-methyl-4,6-dicyclohexenylaniline, yellow oil, b12 230-5° (picrate, m. 176-7°); p-MeC6H4NH2 (110 g.) gives 9 g. of 4-methyl-2,6-dicyclohexenylaniline, b13 228°, m. 60° (picrate, m. 192°; Bz compound, m. 69°). p-Cyclohexylaniline (30 g.) gives about 1 g. of the compound C24H25N, b1 200-5°. 3-Methylcyclohexanone (IV) (50 g.) and 83 g. PhNH2 after 12 days at 100° give 42 g. PhNH2, 24 g. methylcyclohexenylaniline (V), b14 187-90° (Ac derivative, m. 127°; Bz derivative, m. 178°; phenylthiourea, m. 143°), and 38 g. 1,1-diaminodiphenyl-3-methylcyclohexane (VI). b14 285-90° (HCl salt, m. 214°; diphenylthiourea, m. 127°); 40 g. PhNH2 and 80 g. IV, 12 days at 100°, give 14 g. PhNH2, 27 g. V and 74 g. VI. PhNMe2 (100 g.) and 100 g. IV give 28 g. methylcyclohexenyldimethylaniline, b14 194-6°, m. 38° (picrate, m. 162°; methiodide, m. 159°), and 11 g. 1,1-tetramethyldiaminodiphenyl-3-methylcyclohexane, b12 295°, m. 109° (picrate, orange, m. 164°; dimethiodide, m. 186°). o-Methyl-cyclohexanone condenses more slowly than IV and yields probably 2-methylcyclohexenylaniline, b14 160°

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(chloroplatinate, m. 211-2°). Cyclopentanone (20 g.) and 86 g. Ph-NMe2 heated with concd. HCl 10 hrs. at 150° give 20 g. cyclopentenyldimethylaniline (VII), b12 160°, m. 10° (HCl salt, m. 170°; picrate, m. 129°; methiodide, decomps. 180°), and 12 g. 1,1-tetramethyldiaminodiphenylcyclopentane, m. 128° (HCl salt, m. 213°; picrate, m. 181; dimethiodide, decomps. 195°). VII is reduced by Na and EtOH to p-cyclopentyldimethylaniline, b12 156° (HCl salt, m. 175°; picrate, m. 134°; methiodide, m. 179°). In the reaction product of PhNH2 and Me2CO (Homolka, Ger. Pat. 399,141). in addn. to Me2C(C6H4NH2)2 there may be observed a small fraction (about 1%) consisting of isopropenylaniline (VIII), b. 125-30° (pressure not given), which may be obtained in better yields by heating Me2C(C6H4NH2)2 with a few drops of dil. HCl and H2SO4 in vacuo; the distillate consists of PhNH2 and VIII in the ratio of about 2:1. VIII yields a HCl salt, m. 230-5°; a picrate, m. 180°; the Ac deriv., m. 110-1°; the phenylthiourea, m. 137°. VIII, freshly prepd., has d420 1.0320 and is a mobile liquid; on standing 40 hrs. there results a dimer or bisisopropenylaniline (IX), m. 173° (HCl salt, m. 228°; picrate, m. 172°; di-Ac deriv., m. 205°; phenylthiourea, m. 117°; these compds. could not be obtained from the corresponding derivs. of VIII). IX is unsatd. towards KMnO4, and the Ac deriv. is catalytically reduced; the dihydro deriv., m. 121°; sapon. gives the bisisopropylaniline (X), b0.1 205-10°, m. 50-2° (diphenylthiourea, m. 178°; picrate, m. 213°; HCl salt, m. 275°). X, through the diazo. reaction, yields the phenol, C13H22O2, m. 106-7° (Bz deriv., m. 117°; Ac deriv., b1.0 192°). Me2CO and PhNHMe, heated 10 hrs. at 150° with HCl, give 50% of 2,2-dimethylaminodiphenylpropane, b1.5 190°, m. 138° (HCl salt, m. 218°; Ac deriv. m. 139°; diphinylthiourea, m. 170°); distn. with a little acid gives equal parts of PhNHMe and N-methyl-p-isopropenylaniline, b14 123-5° (HCl salt, oily; Picrate, m. 147°); d. 0.9675, changes only to 1.0067 after heating 20 hrs. on the H2O bath, indicating only slight polymerization. Me2C(C6H4-Me2)2 give N-dimethylisopropenylaniline, b15 120-2°, m. 74° (HCl salt, m. 122°, picrate m. 96°); this also shows little tendency to polymerization. Me2CO and m-MeC6H4NH2 give about 9% of 3-methyl-4-isopropenylaniline (XI), b13 150-5° (HCl salt, m. 217°; picrate, m. 224°; Ac compd., oily), reduced to 3-methyl-4-isopropylaniline, b13 141-5° (HCl salt, m. 211°) and 3% of 3-methyl-4,6-diisopropenylaniline, b13 225-30° (HCl salt, m. 218°; picrate., m. 205°). XI, warmed 16 hrs. at 100°, shows about 10% polymerization. 2,2-Diaminodiphenylbutane, b3 210° (20% yield); distd. with a little HCl or H2SO4, there results about 40% of p-isobutenylaniline, b14 140-5°, d419 0.9899 (HCl salt, m. 238°; picrate, m. 196°; phenylthiourea, m. 131°; Ac deriv., m. 121°); after standing 4 days and warming 24 hrs. at 100°, 75% is recovered unchanged while the rest is obtained as a dark red hard glass. 2,2-Dimethylaminodiphenylbutane, b4 240°, m. 98° (diphenylthiourea, m. 142°; di-Ac deriv., m. 121°); p-isobutenylmethylaniline, b14 145-50°. 2,2-Tetramethyldiaminodiphenylbutane, b0.3 210-2° (HCl salt, m. 125°; picrate, m. 80-90°; methiodide, m. 202°); p-isobutenyldimethylaniline, b14 138-42°, d420 0.9561; (picrate, m. 125°; dimethiodide, m. 175°); polymerization is scarley noticeable. MeBuCO and PhNMe3 give 5% p-isohexenyldimethylaniline, b12 160-2° (methiodide, m. 175°), and 15% 2,2-tetramethyldiaminodiphenylhexane, b4 230-4° (dimethiodide, m.

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.196°). PhAc and PhNMe2 give 20% of tetramethyldiaminotriphenyletha
ne, m. 134° (dimethiodide, m. 188°), and 7-8% of
p-α-phenylvinyldimethylaniline, b13 208-11°, d20 1.0409 (HCl
salt, m. 144°; methiodide, m. 170°). Condensation of PhNH2
and PrCHO gives only 2-propyl-3-ethylquinoline; PrCHO and PhNMe2 with 20%
HCl and a little EtOH show about 30% condensation after 5 days at
100°; the principal product is 1,1-tetramethyldiaminodiphenylbutane
, b0.3 225-7°; distd. with a little H2SO4 in vacuo there
results 30% of a mixt. of PhNMe2 and p-butenyldimethylaniline, the latter,
b12 140-2°, d415 0.9395 (picrate, reddish yellow, m.
99-100°); it shows little tendency to polymerize, even on heating
at 100° for 24 hrs.; warming with PhNH2.HCl for 30 hrs. gives about
50% of 1,1-aminophenyl[dimethylaminophenyl]butane, b0.2 205-10°.
In comparison with PrCHO, BzH and PhNMe2 are almost completely condensed
in 24 hrs.; p-Me2NC6H4CHO is completely condensed in 24 hrs. and
p-NO2C6H4CHO in about 18 hrs. In acid soln. 1 mol. of an aromatic
aldehyde and 1 mol. of an aromatic aniline first condense to a very active
product closely related but not identical with the basic hydrol. Condensa
tion of 2 mols. PhOH and 1 mol. cyclohexanone, using 1/3 of the wt. of the
latter of concd. HCl, at 36° gives, after 60 hrs. a 65% yield,
consisting of 1,1-dihydroxydiphenylcyclohexane (XII) (di-Me ether, b16
260-3°, m. 82°; di-Ac deriv., m. 122°) (cf. Schmidlin
and Lang, C. A. 5, 487), and a small amt. of o-
cyclohexylidenecyclohexanone. Distn. of XII at the ordinary
pressure gives PhOH, cyclohexenylphenol (XIII), m. 123° (Me ether,
b14 155°, m. 35°; Ac deriv., m. 52°), and
p-cyclohexenylphenol (XIV), m. 131° (Me ether, m. 58°; Ac
deriv., b15 170°, m. 35°). XIII adds Br to the double bond
before substitution occurs and this reaction may be used to det. the amt.
of XIII present in the mixt. with XIV. Warming XIII with concd. HCl gives
about 50% of XIV, while the other half is a resinous mass, similar to that
obtained by the distn. of XII. Heating XII with Ni and H at
230-50° gives cyclohexanol, p-cyclohexylcyclohexanol (Schrauth and
Gorig, C. A. 18, 388) (Ac deriv., b15 158-60°), and a partial
reduction product of XII, C13H2602, b13 260-70°. Cyclohexanone and
m-MeC6H4OH, after 14 days, condense to the extent of 40%;
cyclohexenylcresol, b12 175°; p-cyclohexyl-m-cresol, thick oil.
o-Methyleyclohexanone and PhOH give methylcyclohexenylphenol, b12
173-5°, and the diphenylmethane compd., C19H2202, b12 280°,
m. 135-7°. Cyclopentanone and PhOH give 1,1-
dihydroxydiphenylcyclopentane, b12 270°, m. 155-6 (Me ether, b12
240-5° m. 115°; Ac deriv., m. 79°); heating with 3
parts concd. HCl 3 hrs. at 100° gives PhOH and p-cyclopentylphenol,
b12 155° m. 63-5° (Me ether, b12 143°; Ac deriv., b12
150-2°); distn. of the diphenol at the ordinary pressure
gives cyclopentenylphenol, m. 148-50° (Me ether, m. 90°; Ac
deriv., m. 72°). 4-Cyclopentylcyclohexanol, b12 135°, m.
43-50° (phenylurethan, m. 115-45°); this is a mixt. of 2
stereoisomers. Oxidation gives 4-cyclopentylcyclohexanone, b12
125°, nD18 1.4860, d418 0.9714 (semicarbazone, m. 195-7°).
Me2CO and PhOH give after 60 hrs. practically quant, Me2C(C6H4OH)2, b13
250-2°; distn. at the ordinary pressure gives a small
amt. of p-isopropylphenol, b12 112-5°, m. 61°; the action of
3 parts of concd. HCl for 20 hrs. at 100° gives a dimer, C18H2002,
b14 255-6°, m. 181°, which is stable towards HCl at
125°; the di-Me ether, m. 115°, is stable towards catalytic
reduction or Na and EtOH; di-Ac deriv., m. 165°. Catalytic
reduction (Ni) gives a mixt. of cyclohexanol, p-isopropylcyclohexanol,
di-4-hydroxycyclohexyldimethylmethane, b14 230-4° (diketone, m.

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158-60°; semicarbazone, m. 222°), and p-hydroxyphenyl
4-hydroxycyclohexyldimethylmethane (XV), b12 244-8° (di-Ac deriv.,
b16 234-7°; mono-Me ether, b1 170-5°). The last 2 compds.
are probably mixts. of stereoisomers. Oxidation of XV with CrO3 gives the
ketone, b15 205-10° (semicarbazone, m. 184°). Oxidation of
XV with KMnO4 gives the substituted adipic acid,
MeOC6H4Me2CCH(CH2CO2H)CH2CH2CO2H, m. 116° (45% yield). Me2CO and
m-MeC6H6OH give the diphenol, b12, 230-5°. MeEtCO and PhOH give a
diphenol, b12 250-3°, which, on distn. at ordinary
pressures, gives, as 1 product, p-isobutenylphenol, m. 86° (Ac
deriv. b15 148°). Catalytic reduction with Ni at 200° gives
the compd., C10H20O, an isomer of menthol, b20 128°, oxidized to
the ketone, C10H18O, b12 104-6° (semicarbazone, m. 190°).
EtCHO and PhOH give EtCH(C6H4OH)3 b15 250°, which, distd.
at atm. pressure, gives p-propenylphenol, m. 89-91°; heating the
latter 1 hr. at its b. p. gives a reddish oil, about half of which is
p-PrC6H4OH. PrCHO gives 1,1-dihydroxydiphenylbutane (XVI), b12
270°, which on distn. gives p-butylphenol, b10
138-41° (Ac deriv., b15 138-41°). Catalytic reduction of
XVI at 220° gives the compd.C16H2402, b15 235-40° (di-Ac
deriv., b14 230-4°), and 4-butylcyclohexanol, b15 120-2°
d420 0.9106, nD15 1.4691, which yields 2 phenylurethans, m. 124°
and 42°, sepd. by crystn. from MeOH; oxidation (CrO3) gives
p-butylcyclohexanone, m. 101-2° (semicarbazone, m. 175°).
PrCHO and m-MeC6H4OH give butenylcresol, b12 150° (Me ether, b12
130-3°; Ac deriv., b12 140°) and 1,1-dihydroxydi-m-
tolylbutane, b12 250° (di-Ac deriv., b11 230-5°); heating 8
hrs. with 3 parts concd. HCl at 120-5° gives 3-methyl-4-
butylphenol, b14 140-5°. Catalytic reduction of MeCH(C6H4OH)2
gives a mixt. of the compd. C14H2002, b12 240° (mono-Me ether,
b0.2 175-8°), and the compd.C14H2602, m. 140-6° (a mixt. of
isomers), oxidized to the ketone, C14H2202, b16 225-30°, m.
55-6° (semicarbazone, m, 215-7°). Camphor (100 g.), 120 g.
PhNH2 and 150 cc. 20% HCl, heated 14 days at 100°, give about 1 g.
of the compd. C14H21N, b0.8 140°, [α]D14 (0.2090 g. in 2.2990
g. EtOH). Similarly 43 g. menthone, 88 g. PhNMe2 and 80 cc. concd. HCl,
heated 10 hrs. at 180°, give 2.5 g. of the compd. C18H27N, b12
195-205°, [α]D16 13° (10% in CHCl3).
d-3-Methylcyclo-pentanone and PhNMe2, heated several days at 100°
in HCl soln., give about 4% of 3-methylpentenyldimethylaniline, m.
64°, which shows scareely any optical activity, and about the same
yield of tetramethyldiaminodiphenyl-3-methylcyclopentane, m. 95°,
[α]D21 22.50° (CHCl3). d-3-Methyleyelohexanone (XVII) and
PhOH, condensed in the usual manner, give 56% of the diphenol, C12H2202,
b2 235-6°, m. 153-5°, [α]D20 -18.74° (EtOH);
heating 4 hrs. at 100° with concd. HCl gives p-methylclohexyl-
phenol, b14 170°, m. 60-75°, [α]D20 -6.94°
(C6H6), identical with that obtained by fractional distn. of the
product obtained by heating 3 hrs. at 100°. XVII and PhNH2 give the
same products as the inactive compd. except that they are optically
active; the diamine has [α]D23 -11.78° (CHCl3), the
unsatd. amine [α]D20 54.21° (EtOH), 57.02°
(CHCl3); a carefully prepd. sample of the diamine, b0.1
240-3°, has [α]D18 -16.21° (CHCl3),
Methyleyelohexylaniline, m. 146°, [α]D17 -4.78 (EtOH);
methylcyclo-hexylphenol, m. 60°, [α]D20 -6.9° (C6H6).
Methylcyclohexenylmethylaniline, b15 192-5°, m, 33°,
[α]D18 47 .6° (CHCl3) (HCl salt, m. 180°);
1,1-dimethylaminophenyl-3-methyl-cyclohexane, b1.5 260-5°,

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[α]D23 -15.26° (CHCl3) (HCl salt, m. 185°;
bisphenylthiourea, m. 105°). The corresponding dimethylaniline
derivs. have [α]D23 46.69° and -20.94°.
3-Methyleyelohexylbenzene (XVIII), b14 123-4°, [α]D20
-5.26° (cf. Kursanov, C. A. 1, 2093). p-
Methyleyelohexylbromobenzene, in 60% yield from the diazo compd. and CuBr,
b14 165-7°, d418 1,2100, [α]D18 -2.23°; the diazo
compd. and CuCN give the nitrile, b14, 166-8°, d413 1.0058,
[α]D26 -1.62°. Reduction of the diazo compd. with SnCl2
gives 50% of p-3-methylcyclohexylphejnylhydrazine, m. 84-5°,
[α]D20 -4.99° (EtOH), relatively unstable (HCl salt, m.
210°; semicarbazide, m. 217-8°; thiosemicarbazide, m.
175°). XVIII and AcCl with AlCl3 give 85% of p-
methylcyclohexylacetaphenone, b14 182-5°, d421 0.9986, [α]D21
-3° (semicarbazone, m. 211°). Methyleyelohexenyl-
methylaniline, m. 33°, yields a yellow NO compd., m. 50°,
reduced to the hydrazine, m. 34° [α]D15 39.12° (EtOH)
(thiosemicarbazide, m. 181°); HCHO gives a hydrazone m.
121°, and BzH a hydrazone, m. 108°.

ACCESSION NUMBER: 1929:40433 CAPLUS
DOCUMENT NUMBER: 23:40433
ORIGINAL REFERENCE NO.: 23:4687g-i,4688a-i,4689a-i,4690a-g
TITLE: Thermal and hydrolytic decomposition of basic and phenolic diphenylmethane derivatives and synthesis of optically active aromatic compounds
AUTHOR(S): v. Braun, Julius; Anton, Ernst; Haensel, Werner; Werner, Georg
SOURCE: Ann. (1929), 472, 1-89
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB If care is taken in the design of the **distillation** apparatus to see that all vapor volatilized passes over into the condenser and collecting flask, the following equation represents the change in composition of the liquid on **distillation**: (log y1 - log y2)/(log x1 - log x2) = k, where x and y refer, resp., to the quantities of water and of volatile organic compound and subscripts 1 and 2 refer, resp., to the quantities at the beginning and end of the **distillation**. By this equation, the purity of a solution of organic compound such as a fatty acid can be proved by the constancy of k in successive **distillation** fractions. The influence of initial concentration and time of **distillation** on the value of k for dilute solns. of formic, acetic, propionic and butyric acids was studied. Concentration affects k only to a slight extent but the time of **distillation** influences k significantly so that it must be kept within close limits in quant. work. The rate of **distillation** adopted was 100 cc. of an original volume of 200 cc. in 60 min. A mixture of 2 volatile compds. e. g. 2 fatty acids, can be analyzed by determining the total acidity of the initial solution and of the **distillate** when half of the solution has passed over, provided that k for each of the acids is known. A mixture of 3 acids can be analyzed by determining the total acidity of initial solution and **distillates** when 1/4 and 1/2 of the sample has passed over. When more than 3 acids are present the exptl. errors become too large. If a compound has a value for k greater than 5 the exptl. errors are too large. Values for k are given for the following acids: formic 0.398, acetic 0.657, propionic 1.270, butyric 2.02, diethylacetic 4.57, chloroacetic 0.047, phenylacetic 0.070, pyruvic 0.074, α-crotonic 0.760, benzoic 0.270, salicylic 0.688, o-toluic 0.508, m-toluic 0.420, p-toluic 0.378, anisic 0.050, cinnamic 0.102, o-aminobenzoic 0.019; m- and p-aminobenzoic and the 3 nitrobenzoic acids do not distil. Approx. values of k for amines are: ammonia 13, **methylamine** 11, **ethylamine** 20, **propylamine** 30, **butylamine** 40, **diethylamine** 43, **ethylenediamine** 0.02, aniline 5.51, methylaniline 16, **benzylamine** 3.25, α-**naphthylamine** 1.05, β- **naphthylamine** very large. For phenols k is: phenol 1.94, p-chlorophenol 1.30, p-nitrophenol 0.005, m-nitrophenol 1.01, thymol 12; for aldehydes: formic 2.6, acetic 40, benzoic 18, anisic 3.1; for alcs.: methyl 8.9, ethyl 12.9. The volatility of a compound with steam increases as the hydration in solution decreases. Neutral salts influence the volatility by altering the hydration, usually decreasing hydration and increasing k. Anions have a greater influence than cations. A given salt has a greater influence on less soluble than on more readily soluble volatile compds. There is a striking parallel between the action of salts on the volatility and on the adsorption of compds. from solution by charcoal.

ACCESSION NUMBER: 1928:36643 CAPLUS
DOCUMENT NUMBER: 22:36643
ORIGINAL REFERENCE NO.: 22:4351f-i,4352a-b
TITLE: The **distillation** of water-soluble organic substances with steam
AUTHOR(S): Virtanen, Artturi I.; Pulkki, L.
SOURCE: Ann. acad. sci. Fennicae (1927), 29A, 28 pp.
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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GI For diagram(s), see printed CA Issue.
AB (Cf. Ibid., 24, 614)-2-Methyl-4-methylaminoheptanol (6) was prepared from α-isomethylheptenone and methylamine and subsequent reduction, and its reactions studied. Experimental. α-Isomethylheptenone, (Ber., 33, 561), (CH3)2CH.CH2.CH:CH.COCH2, and methylamine at -10 to -20°, acidified and then reduced with sodium amalgam on distillation yielded 2-methyl-4-methylaminoheptanol(6), (CH3)2CH.CH2CH(NHCH3).CH2CH(OH).CH3, b13 106-107°. On methylation and with gold chloride, the chloraurate (C9H20NO.CH2.CH3Cl) AuCl2, m. 120°, was found, and with nitrous acid, the nitrosamine was prepared. The aminoalcohol and formaldehyde yielded a tetrahydromethoxazine derivative, (CH3)2CH.CH2CH CH2.CH(CH3) N(CH3).CH2 O, b13 83.5-84°. Chloraurate, m. 130-134°, chlorplatinate, which added methyl iodide at the ordinary temperature, and formed double salts of the methylated product with gold and platinum chlorides. With chlorcarbonic ester the aminoalcohol yielded the lactone of the carbonic acid, (CH3)2CH.CH2.CH CH2.CH(CH3) N(CH3)C.H2 O, b11 170.5°. With ethylene oxide a basic glycol, (CH3)2CH.CH8.CH(CH2.CHOH.CH3).N(CH3).CH2.CH2OH, b13 161-162°, was formed. The aminoalcohol and HBr yielded the hydrobromide of 6-brom-4-methylamino-2-methylheptane, which with alkali produced N-α-dimethyl-γ-isobutyltrimethyleneimine, (CH2)2CH.CH3.CH CH2 N(CH3) CH.CH3, b. 152-154°, picrate, m. 93.94°. Methyl iodide, (the methyl chloride, its chloraurate, m. 63-64°, and chlorplatinate, m. 170-171° with decomposition, were also prepared), treated with alkali yielded a tertiary base, C10H21N, b. 168-71°, chlorplatinate, m. 135-38°, picrate, b. 84-85°, which was unsaturated and of which the methyl iodide (chloraurate of the methyl derivative, m. 75-80°), and its chlorplatinate, m. 155-156° with decomposition, with silver oxide formed the ammonium compound, which on dry distillation yielded H2O, (CH3)3N, and an unsaturated hydrocarbon, C5H14, taking up two atoms of bromine at 0°. The structural formulas of the compounds, C14H21N and C2H24 are not established as yet.
ACCESSION NUMBER: 1907:10756 CAPLUS
DOCUMENT NUMBER: 1:10756
ORIGINAL REFERENCE NO.: 1:2564d-i,2565a
TITLE: The Preparation of Aminoalcohols from Unsaturated Methylketones. II Communication
AUTHOR(S): Kohn, Moritz; Giaconi, Jakov
CORPORATE SOURCE: Univ. Vienna
SOURCE: Monatshefte fuer Chemie (1907), 28, 461-78
CODEN: MOCMB7; ISSN: 0026-9247
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L14 ANSWER 36 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
the para compound. Diphenyl oxalate yields only oxalphenetidide. With resorcinol 1,3-dihydroxybenzylphenetidine, (HO)2C6H3CH2NHC4H4OEt, is formed; irregular, thin plates, m. 156°. In addition to the above methylene bases the action of a number of others on diphenyl oxalate has been studied. Methylaniline gives a mixture of dimethyloxanilide, PhNMeCOCONMePh, colorless crystals, m. 86° and phenyl methyloxanilate, PhNMeCOCO2Ph, oil, b10 about 270°. The "methyloxanilide" of Norton and Livermore (Ber., 20, 2273), b. 249°-251°, cannot be a derivative of oxalic acid, but may, perhaps, be methylformanilide. Phenylhydrazine and diphenyl oxalate give oxalyldiphenylhydrazide, which has been previously prepared by E. Fischer from diethyl oxalate. Phenyl phenyloxanilate, Ph2NCOCO2Ph, from diphenyl oxalate and diphenylamine; prisms, m. 127°-128°. Phenyl benzyloxanilate, PhCH2NPhCOCO2Ph, from diphenyl oxalate and benzylaniline; colorless prisms, m. 93°-94°. Carbazole and diphenyl oxalate could not be induced to interact.
ACCESSION NUMBER: 1907:1663 CAPLUS
DOCUMENT NUMBER: 1:1663
ORIGINAL REFERENCE NO.: 1:416g-i,417a-i
TITLE: Resolution of N, N'-Diarylmethylenediamines
AUTHOR(S): Bischoff, C. A.; Frohlich, E.
CORPORATE SOURCE: Synthetic Lab., Polytechnicum, Riga
SOURCE: Ber. (1907), 39, 3964-81
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L14 ANSWER 36 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB Some years ago the author found that the methylene bases, RNHCH2NHR, unlike the corresponding ethylene derivatives, do not yield closed chain compounds with diphenyl oxalate (Ber., 35, 3440) but hydroxybenzylamine derivatives, HOC3H4CH2NHR, and oxalylarylamides, RNHCOCONHR. In certain cases, however, especially with p-tolyl derivatives, the secondary base is converted into an equimolecular mixture of primary, H2NR, and tertiary base, RN NR, which latter, with phenols, yield the above hydroxybenzylamine compounds. Phenol and the secondary methylene bases give phenol salts of primary bases, PhONH2R and a mixture of the components. The methylene usually enters the phenol ring in the ortho position, but in the case of orthomethoxybenzene and parasethoxybenzene the methylene enters at the para position. In the above cases R = C6H6, o-C4H4CH6, o-C4H4CH3, o-C4H4OCH3, p-C3H4OCH3, p-C6H4OC2H5. N,N'-Diphenylmethylenediamine, PhNH.CH2NHPh. This base gives, with phenol, a hydroxybenzylaniline, microscopic prisms, m. 156° and also the ortho isomeride, m. 113°, which is likewise formed from phenol and "anhydroformaldehyde aniline." Resorcinol yields a 1,3-dihydroxybenzylaniline, (HO)2C4H3CH2NHPh, crystalline powder consisting of small rods. It could not be benzoylated. Diphenyl oxalate gives oxanilide and o-hydroxybenzylaniline. Sodium phenolate resolves the base into aniline. The base does not react with acetone, alcoholic potassium hydroxide, ethyl acetate, or benzaldehyde. Ethyl oxalate, ethyl malonate and ethyl succinate, on the other hand, yield the anilides of the respective acids and a mixture of tertiary "anhydro" bases. N,N'-Diorthotolylmethylenediamine. Prepared from o-toluidine hydrochloride and formaldehyde by an improved method. Yield, 50%. Aniline, under the same conditions, gives only mixtures of "anhydroformaniline." With phenol the above base gives, in very small quantity, what is probably o-hydroxybenzyl-o-toluidine; transparent plates, m. 40°-50°. Diphenyl oxalate yields oxal-o-anilide, m. 210°. N,N'-Diparatolylmethylenediamine. With phenol o-hydroxybenzyl-p-toluidine is formed. Resorcinol yields m-dihydroxybenzyl-p-toluidine, (HO)2C6H3CH2NHC3H4Me, microscopic rods or plates, m. 165°. Diphenyl oxalate gives oxal-p-toluide and "anhydroformtoluidine," a mixture of tertiary bases, m. 127°-128° and 212°-223°, respectively. (vide Ber., 31, 3253). N,N'-Diorthoanisylmethylenediamine. The base b20 160°; distillation with phenol does not cause a reaction. At 180°-200° a hydroxybenzyl-o-onisidine, is formed, microscopic rods, m. 125°. It is probably the p-compound. The ortho isomer was also obtained by boiling the reacting substances in benzene. With diphenyl oxalate, oxalo-o-anisidide is formed, hexagonal plates, m. 246°. It was prepared for comparison from diphenyl oxalate and o-anisidine. p-Nitrophenol, pyrocatechol, resorcinol and hydroquinol could not be induced to act on this diamine and all attempts to prepare an "anhydro base" were fruitless. N,N'-Diparaanisylmethylenediamine. Phenol and p-anisidine combine, in ligroin solution, forming the phenolate, C18H16O2N, colorless prisms, m. 60°. With the methylene base phenol yields o-hydroxybenzylanisidine. Diphenyl oxalate forms oxanisidide and resorcinol gives 1,3-dihydroxy-p-anisidine, (HO)2C6H2CH2NHC3H4OMe, colorless thin plates, m. 149°; at 140° it becomes red. N,N'-Diparaphenetylmethylenediamine, b12 174°; boiling in air resolves it into its constituents. No formation of tertiary base could be observed. Phenol and phenetidine yield the phenolate, long, lustrous needles, m. 52°. Phenol and the methylene base give a mixture of products, but in benzene solution a hydroxybenzyl-p-phenetidine is formed; small prisms, m. 106°. It becomes yellow in air and is probably

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=>  s secondary
        410236 SECONDARY
          1798 SECONDARIES
L15     411299 SECONDARY
                 (SECONDARY OR SECONDARIES)

=> d his

     (FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005)

     FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005
L1            1 S FORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005
L2        61794 S 50-00-0/RN
L3       166261 S N-METHYL?
L4      1415128 S ?AMINE
L5          889 S L2 AND L3 AND L4
L6       362618 S DISTILL?
L7           47 S L5 AND L6
L8       135208 S FORMALDEHYDE
L9        53548 S L8 AND L2
L10      143454 S L8 OR L2
L11        3718 S L10 AND L3
L12        2315 S L11 AND L4
L13        2268 S L12 NOT L7
L14          36 S L13 AND L6
L15     411299 S SECONDARY

=> s l15 and l9
L16       1271 L15 AND L9

=> s l16 and l6
L17         72 L16 AND L6

=> s l17 not l7
L18         65 L17 NOT L7

=> s l18 not l14
L19         65 L18 NOT L14

=> d l19 1-65 abs ibib
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L19 ANSWER 1 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB A process for the preparation of 1-substituted-4-substituted-aminomethyl-1,4-pentadien-3-ones (I; e.g., 1-p-anisyl-4-piperidinomethyl-1,4-pentadien-3-one), useful as anti-H.I.V. and spermicidal agents, comprises: (i) heating a 1-substituted-1-buten-3-one (e.g., cis- and trans-p-anisylideneacetone) with a **secondary** amine (e.g., piperidine) or its salts and a **formaldehyde** solution in the presence of a lower C2-3 aliphatic alc. (e.g., ethanol); (ii) removing the aliphatic alc. by **distillation** under reduced pressure; (iii) neutralizing the obtained residue with an aqueous alkali bicarbonate (e.g., sodium bicarbonate) solution; (iv) extracting the reaction mixture with an organic solvent; (v) evaporating off the solvent; (vi) chromatographing the residue; (vii) heating the obtained 1,5-disubstituted-1-penten-3-one (e.g., 1-p-anisyl-4-piperidinomethyl-1-but-3-one) with paraformaldehyde in the presence of a C2-4 aliphatic acid (e.g., acetic acid); (viii) removing the aliphatic acid by vacuum **distillation**; (ix) neutralizing the residue with an aqueous alkali bicarbonate solution; (x) extracting the reaction mixture with an organic solvent; (xi) evaporating off the solvent; and (xii) chromatographing the residue to obtain I.

ACCESSION NUMBER: 2004:1044567 CAPLUS
DOCUMENT NUMBER: 141:424110
TITLE: Process for the preparation of 1-substituted-4-substituted-aminomethyl-1,4-pentadien-3-ones useful as anti-H.I.V. and spermicidal agents
INVENTOR(S): Khanna, Nandoo Mal; Dwivedi, Anil Kumar; Pal, Raghwendra; Singh, Satyawan; Setty, Bachu Srinivasulu; Kambaj, Veo Prakash
PATENT ASSIGNEE(S): Council of Scientific and Industrial Research, India
SOURCE: Indian, 14 pp.
CODEN: INXXAP
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
IN 186313	A	20010804	IN 1996-DE2629	19961129
PRIORITY APPLN. INFO.:			IN 1996-DE2629	19961129
OTHER SOURCE(S):	CASREACT 141:424110			

L19 ANSWER 2 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB A method of separation of lower aliphatic acids from aqueous solns. containing formic acid comprises reacting a mixture of lower aliphatic acids with amines in the presence of **formaldehyde** and subjecting the resulting salts to thermal decomposition with simultaneous **distillation** of the acids. The invention makes use of removing formic acid from the aqueous solns. of lower carboxylic acids by reductive alkylation of primary and **secondary** amines in the presence of **formaldehyde**. Formic acid is removed from the initial mixture by adding (i) 0.5-0.53 mol of primary amines or 1.0-1.03 mol of **secondary** amines of the general formula R1R2NH, where R1 is an aliphatic hydrocarbon radical with 6-25 carbon atoms, and R2 is hydrogen or an aliphatic hydrocarbon radical with 1-25 carbon atoms, and (ii) 1.0-1.03 mol of **formaldehyde** per 1 mol of formic acid, the process being carried out at 50-80°. Tertiary amines formed during the process form salts with the carboxylic acids present in the solution, addnl. amount of pure tertiary amines being added to provide complete conversion to salts.

ACCESSION NUMBER: 2003:444608 CAPLUS
DOCUMENT NUMBER: 140:130112
TITLE: Method of separation of lower aliphatic acids from aqueous solutions containing formic acid
INVENTOR(S): Fakhretdinov, P. S.; Romanov, G. V.; Mizipov, I. R.
PATENT ASSIGNEE(S): Institut Organicheskoi i Fizicheskoi Khimii im. A. E. Arbuzova Kazanskogo Nauchnogo Tsentra RAN, Russia
SOURCE: Russ., No pp. given
CODEN: RUXXE7
DOCUMENT TYPE: Patent
LANGUAGE: Russian
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
RU 2197471	C1	20030127	RU 2001-117948	20010628
PRIORITY APPLN. INFO.:			RU 2001-117948	20010628
OTHER SOURCE(S):	MARPAT 140:130112			

L19 ANSWER 3 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Removal of trimethylolpropane formate from trimethylolpropane (I), as produced by the hydrogenation of 2,2-dimethylolbutanal, is achieved by drying the raw solution of hydrogenation product and addition of ammonia or primary and/or **secondary** amines in anhydrous form. Thus, PrCHO was condensed with aqueous HCHO in the presence of Et3N at 40°, and the lower-boiling reactants and byproducts were removed in a thin-film evaporator and recycled. The heavier fraction was passed through a second-stage reaction with addnl. Et3N in a tubular reactor at 40° and the product was hydrogenated over a catalyst containing Cu 20, CuO 24, and TiO2 46% and H2O was **distilled** to give a crude I fraction containing 82% I and 7% I monoformate. The crude I was mixed with Me2NH and heated at 120° for 34 min to give complete conversion of the I monoformate to addnl. I, as well as DMF.

ACCESSION NUMBER: 2001:489340 CAPLUS
DOCUMENT NUMBER: 135:93381
TITLE: Method for the conversion of trimethylolalkane formate arising during manufacture of trimethylolalkane
INVENTOR(S): Dernbach, Matthias; Kratz, Detlef; Stammer, Achim; Schulz, Gerhard
PATENT ASSIGNEE(S): BASF A.-G., Germany
SOURCE: PCT Int. Appl., 24 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001047849	A1	20010705	WO 2000-EP13327	20001228
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
DE 19963444	A1	20010712	DE 1999-19963444	19991228
PRIORITY APPLN. INFO.:			DE 1999-19963444 A	19991228
REFERENCE COUNT:	4	THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT		

L19 ANSWER 4 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Trimethyolalkanes (e.g., trimethylolpropane) are prepared in high yield and selectivity by the reaction of alkanals (e.g., n-butyraldehyde) and **formaldehyde** in the presence of a tertiary amine (e.g., triethylamine) and water, followed by a step for the **distillation** of the tertiary amine and water such that the **formaldehyde**-alkanal reaction mixture is heated so that formate byproduct salts (e.g., triethylammonium formate) of the tertiary amine are thermally dissociated, and the formate ester byproducts of the trimethylolalkane in the residue are reacted with water and a primary or **secondary** amine to produce the corresponding formamides which are easily removed from the trimethyolalkane product.

ACCESSION NUMBER: 1999:286252 CAPLUS
DOCUMENT NUMBER: 130:282806
TITLE: Method for the high-yield preparation of trimethyolalkanes from the reaction of alkanals and **formaldehyde**
INVENTOR(S): Doi, Kenji; Jinno, Takuhiko; Moriyama, Ayao; Uji, Shingo
PATENT ASSIGNEE(S): Koei Chemical Co., Ltd., Japan
SOURCE: Ger. Offen., 8 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 19848568	A1	19990429	DE 1998-19848568	19981021
CN 1219527	A	19990616	CN 1998-120446	19981020
CN 1116262	B	20030730		
US 6034284	A	20000307	US 1998-175431	19981020
SG 79241	A1	20010320	SG 1998-4230	19981020
IT 1305123	B1	20010410	IT 1998-TO888	19981020
IT 98TO0888	A1	19990422		
TW 555741	B	20031001	TW 1998-87117387	19981021
JP 11199531	A2	19990727	JP 1998-301428	19981022
PRIORITY APPLN. INFO.:			JP 1997-309232 A	19971022
			JP 1997-327059 A	19971111

L19 ANSWER 5 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB An increasing number of publicly owned treatment works (POTWs) are reporting difficulties in complying with cyanide permit levels set by their states and some are facing legal action by public challengers in the light of being unable to control these apparent permit violations. Part of this problem is the impossible burden placed on utilities and their contract anal. labs. to determine cyanide levels often at or below the practical quantitation limit of 10 μg/L set by the US EPA for the currently approved anal. methodol. The methodol. is cumbersome, unreliable, and in many cases fails to effectively recover measured addns. of cyanide in the matrix being analyzed. There have been instances of apparent levels of cyanide in the chlorinated effluents of plants that had no measurable level in their secondary effluents. An alternative technique to the existing EPA approved methodologies should take advantage of modern separation techniques using automation and providing for rapid sample throughput with the minimal of sample handling. We evaluated an alternative procedure for the anal. of total cyanide in wastewaters which utilizes segmented flow injection for sample transport and reaction, on line acidic UV digestion for conversion of complexed cyanide to HCN, and amperometric detection achieved within 4 min of sample injection. Grab samples were collected from different points in a variety of wastewater treatment plants and split for simultaneous anal. of total cyanide at 3 different labs. Samples were analyzed by both the standard EPA method and the FIA method developed here. The application of this latter methodol. to the anal. of wastewaters compares favorably with the traditional methodol. when the latter is used under strict quality control protocols. However, when high cyanide values were obtained using the distn ./colorimetric approach (EPA method), they were also obtained with the flow injection method. This paper reports the procedures to minimize cyanide formation during wastewater treatment and the subsequent anal. Guidance is provided for appropriate sample handling, screening, and processing in order to assure valid anal. results.

ACCESSION NUMBER: 1999:256487 CAPLUS
DOCUMENT NUMBER: 130:342628
TITLE: Application of flow injection for the analysis of total cyanide in wastewater treatment plant effluents
AUTHOR(S): Weinberg, H. S.; Cook, S. J.; Singer, P. C.
CORPORATE SOURCE: Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27599-7400, USA
SOURCE: Proceedings - Water Environment Federation Annual Conference & Exposition, 71st, Orlando, Fla., Oct. 3-7, 1998 (1998), Volume 1, 237-246. Water Environment Federation: Alexandria, Va.
CODEN: 67NFAZ
DOCUMENT TYPE: Conference
LANGUAGE: English
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L19 ANSWER 6 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Title process is carried out by previously treating methacrylic acid-containing materials (prepared by vapor-phase contact oxidation of C4 compds.) with primary and/or secondary amino group-containing compds., treating with strongly acidic cation exchange resins, then mixing with formaldehyde-containing materials, flowing through a strongly acidic cation exchange resin-charged fixed bed, and distilling the treated product. Thus, 100 g crude methacrylic acid (prepared by vapor-phase contact oxidation of isobutylene; color number APHA63; purity 99.2%) was treated with 0.05 g ethylenediamine in the presence of 0.05 g phenothiazine, simple-distilled, treated with 2.5 g Amberlyst 15E (strongly acidic cation exchange resin) in the presence of 0.02 g hydroquinone, freed of Amberlyst 15E, mixed with 100 ppm formaldehyde, flowed through an Amberlyst 15E-charged fixed bed, and simple-distilled to give purified methacrylic acid (recovery 96%; color number APHA3).

ACCESSION NUMBER: 1999:142347 CAPLUS
DOCUMENT NUMBER: 130:197101
TITLE: Purification process of methacrylic acid for purified product with less discoloration and good performance of polymerization
INVENTOR(S): Yoshida, Koichi; Kobayashi, Yoshiaki; Okita, Motomu
PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 11060536	A2	19990302	JP 1997-216119	19970811
PRIORITY APPLN. INFO.:			JP 1997-216119	19970811

L19 ANSWER 7 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB 1,3-Dioxolane (I) is prepared by treatment of ethylene glycol (II) with HCHO or substances generating HCHO in the presence of acid catalysts, distillation of the reaction mixts., concentration of the distillates with or after addition of alkali substances, treatment of the concentrated solns. with C1-4 alkyl-substituted benzene to extract I, and distillation of the exts. to remove low-b.p. impurities and the extraction solvents. II was treated with aqueous HCHO and H2SO4 at 115°, distilled, further distilled with feeding aqueous NaOH, extracted with MePh, and distd. to give high-purity I.

ACCESSION NUMBER: 1998:498639 CAPLUS
DOCUMENT NUMBER: 129:122656
TITLE: Preparation and purification of 1,3-dioxolane
INVENTOR(S): Kuriyama, Ikuhisa; Kondo, Takao; Nakatani, Daigo; Yamada, Kenji
PATENT ASSIGNEE(S): Mitsubishi Gas Chemical Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 10204080	A2	19980804	JP 1997-12741	19970127
PRIORITY APPLN. INFO.:			JP 1997-12741	19970127
OTHER SOURCE(S):	MARPAT 129:122656			

L19 ANSWER 8 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Treating RCH2CHO (I; R = H, hydrocarbyl) with formaldehyde in an aqueous medium in the presence of a C6-8 secondary amine and a C6-12 aliphatic carboxylic acid gives title compds. RC(:CH2)CHO and the amine and the acid are recovered and recycled. Thus, propionaldehyde, 37% formalin, di-n-butylamine (II), and caprylic acid (III) were fed continuously into an autoclave under N at 130° and 40 kg/cm2, the reaction mixture was collected under ice cooling and distilled to recover methacrolein (in 94.8% yield) together with H2O from the top, the bottom containing II and III was mixed with NaOH and distilled to recover 72% of II, and the residue was mixed with 20% H2SO4 and hexane to recover 98% of III from the organic layer.

ACCESSION NUMBER: 1995:275379 CAPLUS
DOCUMENT NUMBER: 122:132585
TITLE: Manufacture of α-methylenealdehydes
INVENTOR(S): Nagareda, Katsushi; Yoshimura, Noriaki
PATENT ASSIGNEE(S): Kuraray Co, Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 06263683	A2	19940920	JP 1993-52485	19930312
JP 3324820	B2	20020917		
PRIORITY APPLN. INFO.:			JP 1993-52485	19930312
OTHER SOURCE(S):	MARPAT 122:132585			

L19 ANSWER 9 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The title compound [(MeO)2P(O)CH2NH]2C:NCN is prepared by phosphonomethylation of cyanoguanidine with (MeO)2POH and HCHO in the presence of a catalyst, such that in order to avoid secondary reactions the HCHO and cyanoguanidine are introduced to the di-Me phosphite as a PhMe solution in a molar ratio of 2:1:2, with holding of the suspension at 55-60° and addition of MeONa in MeOH (447 g/L) to cause an exotherm; the water formed during the reaction is removed as an azeotrope with MeOH by distn., raising the temperature of the reaction mass to 70-80° for 3-5 h. In an example, 170 g of the desired product is obtained from 0.5 mol cyanoguanidine.

ACCESSION NUMBER: 1994:680882 CAPLUS
DOCUMENT NUMBER: 121:280882
TITLE: Preparation of tetramethyl cyanoguanidinobis(methanediphosphonate)
INVENTOR(S): Petrov, Pavel; Braitiu, Melania
PATENT ASSIGNEE(S): Intreprindera Textila, Timisoara, Rom.
SOURCE: Rom., 3 pp.
CODEN: RUXXA3
DOCUMENT TYPE: Patent
LANGUAGE: Romanian
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
RO 103190	B1	19920613	RO 1988-136908	19881224
PRIORITY APPLN. INFO.:			RO 1988-136908	19881224

L19 ANSWER 10 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB α-Alkylacroleins CH2:CR1CHO (I; R1 = H, C1-10 alkyl, allyl) are prepared by reacting R1CH2CHO with HCHO (II) in the presence of a primary or secondary amine (0.01-10.0 equiv/1 mol I) catalyst having buffer capability. The reaction is carried out at 20-150°, 0.1-50 atom, and pH 2.5-12.0. New catalysts found such as amine salts of boric acid, phosphoric acid, carboxylic acids, and carbonic acid (derivs.) are free from environmental problems and the process gives I of excellent stability in high yields and selectivity under relatively mild conditions in a short reaction time. Thus, a solution of an oxalic acid amine salt was formed from 1260 parts (10 mol) oxalic acid dihydrate, 1050 parts (10 mol) (HOCH2CH2)2NH, and 2000 parts H2O, thereto 857 parts (10 mol) 35% aqueous HCHO and 580 parts (10 mol) MeCH2CHO were added, and the mixture was kept at 60° for 5 min to give after separation and distillation 92.6% methacrolein. No polymerization was observed after keeping the product at 20° for 2 days.

ACCESSION NUMBER: 1993:212487 CAPLUS
DOCUMENT NUMBER: 118:212487
TITLE: Preparation of α-alkylacroleins by Mannich reaction
INVENTOR(S): Nakano, Tatsuya; Komoritani, Masahiro
PATENT ASSIGNEE(S): Daicel Chemical Industries, Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 15 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 04338355	A2	19921125	JP 1991-111588	19910516
JP 2945165	B2	19990906		
PRIORITY APPLN. INFO.:			JP 1991-111588	19910516
OTHER SOURCE(S):	CASREACT 118:212487; MARPAT 118:212487			

L19 ANSWER 11 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB In preparation of the title compds. by treating corresponding 1 mol part R1CH2CHO (I; R1 = H, C1-10 alkyl) with 1-1.5 mol part HCHO in the presence of catalysts containing organic carboxylic acids (C) and secondary amines (A) at equivalent ratios of C/I 1-5 and C/A 0.5-2, the reaction is conducted at 30-120° in completely stirred tank reactors until 50-90% I-conversion at the 1st step, subsequently at 30-120° in piston-flow type reactors to complete the reaction at the 2nd step, followed by distillation of reaction solns. at 80-150° in decomposition column to give the title compds. A completely stirred tank reactor was fed with aqueous HCHO 1, EtCHO 1, EtCO2H 2, Bu2NH 2 mol, and H2O at 90° for 30 min (85% I conversion), the reaction solns. were fed into a piston-flow type reactor at 90° for 20 min to complete the reaction, the obtained reaction solns. were distilled at 105° for 20-25 min in a decomposition column to give 69.3 g methacrolein.

ACCESSION NUMBER: 1992:591335 CAPLUS
DOCUMENT NUMBER: 117:191335
TITLE: Preparation α-alkylacroleins
INVENTOR(S): Matsuoka, Kazuyuki
PATENT ASSIGNEE(S): Daicel Chemical Industries, Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 5 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 04173757	A2	19920622	JP 1990-300135	19901106
PRIORITY APPLN. INFO.:			JP 1990-300135	19901106
OTHER SOURCE(S):	MARPAT 117:191335			

L19 ANSWER 12 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB 2-Methylalkanals are obtained from mixts. of isomeric aldehydes (from hydroformylation of isomeric olefins) by distillation in the presence of HCHO and an aldol reaction catalyst. Thus, an aldehyde mixture (from Rh-catalyzed hydroformylation of crude 2-methyl-1-butene) containing 2,3-dimethylbutanal (I) 69.57, 3-methylpentanal (II) 21.13, and 4-methylpentanal (III) 7.46 weight% was treated with formalin, Bu2NH, and PrCO2H and fractionally distilled at 0.1 MPa. Of 5 fractions, the 2nd containing 79.9% of the original I had a composition of I 97.14, II 0.01, and III 1.24% by gas chromatog.

ACCESSION NUMBER: 1990:138600 CAPLUS
DOCUMENT NUMBER: 112:138600
TITLE: Preparation of 2-methylalkanals from mixtures of isomeric aldehydes by treatment with formaldehyde
INVENTOR(S): Weber, Juergen; Lappe, Peter; Springer, Helmut
PATENT ASSIGNEE(S): Hoechst A.-G., Fed. Rep. Ger.
SOURCE: Eur. Pat. Appl., 7 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 335221	A2	19891004	EP 1989-104991	19890321
EP 335221	A3	19900207		
EP 335221	B1	19931229		
R: CH, DE, FR, GB, IT, LI, NL, SE				
DE 3811039	A1	19891019	DE 1988-3811039	19880331
CA 1313680	A1	19930216	CA 1989-594386	19890321
JP 01287050	A2	19891117	JP 1989-76885	19890330
JP 06078261	B4	19941005		
US 5064508	A	19911112	US 1990-574609	19900828
PRIORITY APPLN. INFO.:			DE 1988-3811039 A	19880331
			US 1989-325660 B1	19890320
OTHER SOURCE(S):	CASREACT 112:138600; MARPAT 112:138600			

L19 ANSWER 13 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB In the manufacture of tertiary amines by the reaction of primary or secondary amines with HCHO in the presence of a hydrogenation catalyst, the reaction product is distilled after the addition of a primary or secondary amine. This method yields a high purity product with reduced discoloration and improved storage stability. Thus, pentamethyldiethylenetriamine, obtained by the reaction of diethylenetriamine with 37% HCHO, in the presence of Pd(5%)/C under H, was mixed with triethylenepentaamine and distilled to give a product with ≥99.0% purity which had color APHA 10 as prepared, and 100 after 3 mo storage at 60°, vs. APHA 50 as prepared and 300 after 10 days for a control distilled without the addition of an amine.

ACCESSION NUMBER: 1987:140108 CAPLUS
DOCUMENT NUMBER: 106:140108
TITLE: Tertiary amines
INVENTOR(S): Torimoto, Yoshiaki; Yokota, Yukinaga; Hashiba, Ikizo; Matsutani, Kazuto
PATENT ASSIGNEE(S): Kao Corp., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 61236751	A2	19861022	JP 1985-77770	19850412
PRIORITY APPLN. INFO.:			JP 1985-77770	19850412

L19 ANSWER 14 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Methacrylic acid (I) [79-41-4] prepared by gas-phase oxidation of C4 compds. was purified by treating with HCHO [50-00-0], H2SO4 or a sulfonic acid derivative, and optionally a primary secondary amine. Thus, 1 kg 98.5% I (by oxidation of isobutane, APHA color 77) was treated with phenothiazine 0.5, 98% H2SO4 0.5, and formalin 1 g at 60° for 10 min and distilled at 30 torr to give I (yield 99.5%, APHA color 10) having polymerization induction period (in the presence of 2,2'-azobis(2-amidinopropane).2HCl, 65°) 3 min, compared with 22 min before the purification

ACCESSION NUMBER: 1984:407785 CAPLUS
DOCUMENT NUMBER: 101:7785
TITLE: Purification of methacrylic acid
PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 59048437	A2	19840319	JP 1982-158824	19820914
JP 03003645	B4	19910121		
PRIORITY APPLN. INFO.:			JP 1982-158824	19820914

L19 ANSWER 15 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB In the preparation of aminopolyacetic acid alkali salts from a mixture of primary or secondary amines, theor. quantity of HCN, HCHO, and aqueous alkali hydroxide, a mixture of HCN(1) and aqueous HCHO (maintained at -10 to 30°) was added to the reactor and the resulting reaction mixture was heated at 60-150°. Thus, 5° HCN(1) 0.67/min and 30° 37% aqueous HCHO 1.85 part/min was introduced from the bottom of a reactor containing 50% aqueous NaOH 384, H2O 150, and (H2NCH2)2 60 parts and maintained at 90° for 3 h to give, after azeotropic distillation of by-product NH3, 93.0% EDTA Na salt vs. 92.0% yield if the 37% aqueous HCHO was introduced from the top of the reactor sep.

ACCESSION NUMBER: 1983:107774 CAPLUS
DOCUMENT NUMBER: 98:107774
TITLE: Aminopolyacetic acid alkali salts
PATENT ASSIGNEE(S): Nitto Chemical Industry Co., Ltd., Japan
SOURCE: Jpn. Tokkyo Koho, 5 pp.
CODEN: JAXXAD
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 57045425	B4	19820928	JP 1976-102534	19760830
PRIORITY APPLN. INFO.:			JP 1976-102534	19760830

L19 ANSWER 16 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Organic compds. present at >10 μg/mL in 4.5M H2SO4 were separated, identified, and determined These compds. were solubilized from Pb-acid battery separators, made of phenol-formaldehyde resin-impregnated cellulose, by the action 4.5M H2SO4 at 75° for 20 h. Separation techniques include: steam distillation, ion-exchange, TLC, gas chromatog., centrifugation, chemical precipitation, paper chromatog., and reverse-phase high-performance liquid chromatog. Identification and quantitation involved the use of gas chromatog., IR, NMR, UV-visible and "total carbon" anal. Glucose, formaldehyde, acetic acid, and formic acid are among the many products found in the leach acid.

ACCESSION NUMBER: 1979:482595 CAPLUS
DOCUMENT NUMBER: 91:82595
TITLE: Analysis of 4.5 mol/L sulfuric acid for organic compounds leached from battery separators
AUTHOR(S): Laird, Edwin C.; Hanna, Samir B.
CORPORATE SOURCE: Globe-Union Inc., Milwaukee, WI, 53201, USA
SOURCE: NBS Special Publication (United States) (1979), 519(Trace Org. Anal.: New Front. Anal. Chem.), 797-802
CODEN: XNBSAV; ISSN: 0083-1883
DOCUMENT TYPE: Journal
LANGUAGE: English

L19 ANSWER 17 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
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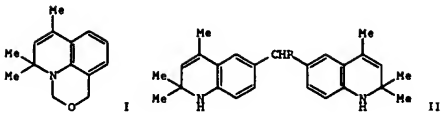

AB The condensation products of 2,2,4-trimethyl-1,2-dihydroquinoline with HCHO [e.g., I and II (R = H)] and MeCHO [e.g., II (R = Me)] were separated by
liquid chromatog. and identified by off-line mass spectroscopy. To avoid secondary reactions the chromatog. eluate was thinly spread over glass wool or over the walls of a glass vessel, vacuum evaporated, and then steam distilled into the mass spectrometer at 10-15 torr. The 400-500 mol.-weight products were steam distilled at 10-5 torr without decomposition

ACCESSION NUMBER: 1979:439285 CAPLUS
DOCUMENT NUMBER: 91:39285
TITLE: Separation and investigation of some heat-sensitive high molecular weight compounds. A combined application of liquid chromatography and mass spectrometry
AUTHOR(S): Fekete, Jeno; Balla, Jozsef
CORPORATE SOURCE: Budapesti Musz. Egy., Budapest, Hung.
SOURCE: Magyar Kemiai Folyoirat (1979), 85(3), 104-11
CODEN: MGKFA3; ISSN: 0025-0155
DOCUMENT TYPE: Journal
LANGUAGE: Hungarian

L19 ANSWER 18 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Lacquer binders were prepared by the reaction of epoxy resins with Mannich bases (prepared from bisphenol A [80-05-7], secondary amines, and HCHO [50-00-0]) and used in electrophoretic coating compns. Thus, a mixture of bisphenol A 1100, diethanolamine [111-42-2] 833.5, bis(2-methoxyethyl)amine [111-95-5] 411.5, and 2-propanol 375 parts was treated slowly with 921 parts 40% formalin, and 2-propanol and water were distilled to prepare a Mannich base (92.5% solids) which (2473 parts) was treated with 57 parts paraformaldehyde at 70°, treated (500 parts) at 60° with 95 parts bisphenol A-epichlorohydrin copolymer [25068-38-6] and 36 parts Epikote 162 [30973-88-7] in 60 parts 1,2-dimethoxyethane, mixed with 18 parts AcOH and 1 l. water to give a 35% resin solution, mixed (810 parts) with 30 parts 50% polyacrylate, used for electrophoretic coating, and baked at 180° for 20 min. to give coatings resistant to salt spray.

ACCESSION NUMBER: 1975:517206 CAPLUS
DOCUMENT NUMBER: 83:117206
TITLE: Lacquer binders
INVENTOR(S): Kempten, Fritz E.; Spoor, Herbert
PATENT ASSIGNEE(S): BASF A.-G., Fed. Rep. Ger.
SOURCE: Ger. Offen., 17 pp. Addn. to Ger. Offen. 2,357,075.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2320301	A1	19750410	DE 1973-2320301	19730421
DE 2320301	C3	19791004		
DE 2320301	B2	19790208		
ZA 7402466	A	19750528	ZA 1974-2466	19740418
BE 813979	A1	19741021	BE 1974-143437	19740419
NL 7405364	A	19741023	NL 1974-5364	19740419
NL 158539	B	19781115		
FR 2226445	A1	19741115	FR 1974-13742	19740419
FR 2226445	B1	19790216		
BR 7403157	A0	19741203	BR 1974-3157	19740419
AT 7403279	A	19760515	AT 1974-3279	19740419
AT 334480	B	19760125		
GB 1457932	A	19761208	GB 1974-17195	19740419
IT 1011253	A	19770120	IT 1974-50504	19740419
SE 409334	C	19791122	SE 1974-5336	19740419
SE 409334	B	19790813		
ES 425531	A1	19760601	ES 1974-425531	19740420
JP 50013499	A2	19750212	JP 1974-44617	19740422
JP 57031574	B4	19820706		

PRIORITY APPLN. INFO.: DE 1973-2320301 A 19730421

L19 ANSWER 19 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The waste water containing HCHO and PhOH was passed through a solvent extractor to remove PhOH, mixed with .apprx.4-6 moles NH3 per mole of the residual HCHO, fed into a primary condenser to remove the excess water as vapor, mixed with 1/6-1/2 mole PhOH per mole of the residual HCHO and fed together with mother liquors produced in the following processes into a crystallizer. The adduct crystals produced were separated and taken out, while the mother liquors were fed into a secondary condenser to take out sludges and returned to the crystallizer, while the distd . liquids from the secondary condenser were returned to the solvent extractor. The staining materials were completely recovered.

ACCESSION NUMBER: 1975:484466 CAPLUS
DOCUMENT NUMBER: 83:84466
TITLE: Treatment of waste water in manufacturing processes for phenol resins
INVENTOR(S): Sawabe, Teruo; Kurachi, Teruo
PATENT ASSIGNEE(S): Sumitomo Bakelite Co., Ltd.
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 49128092	A2	19741207	JP 1973-40041	19730410

PRIORITY APPLN. INFO.: JP 1973-40041 A 19730410

L19 ANSWER 20 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Liquid or low m.p. solid methylene-bridged polyarylamines with a large proportion of 2,2' and 2,4' links, useful as curing agents in thermoset or thermoplastic polyurethane cast plastics, were manufactured from secondary or tertiary arylamines and formaldehyde [50-00-0] without catalyst or with a weak acid catalyst at >120.deg.. Thus, 3.75 parts NaCl was added to a mixture of 428 parts N-methylaniline [100-61-8] and 81.1 parts 36.5% aqueous tech. HCHO which was polymerized 6 hr at 192-6.deg.. A brown oil was isolated containing .sim.66% N,N'-dimethyldiaminodiphenylmethanes and formaldehyde -N-methylaniline copolymer. The distillate from the oil at 0.8 mm and b.p. 195-210.deg. was a yellow oil containing 2,2'-bis(N-methylamino)diphenylmethane, 2,4'-bis(N-methylamino)diphenylmethane, and 4,4'-bis(N-methylamino)diphenylmethane in a 1:5.5:13.8 ratio.

ACCESSION NUMBER: 1974:404352 CAPLUS
DOCUMENT NUMBER: 81:4352
TITLE: Methylene bridged polyarylamines
INVENTOR(S): Brooks, Martin Frederick; Kerrigan, Vincent
PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.
SOURCE: Brit., 10 pp.
CODEN: BRXXAA
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 1341018	A	19731219	GB 1970-10428	19710419

PRIORITY APPLN. INFO.: GB 1970-10428 A 19710419

L19 ANSWER 21 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The title compds. were prepared by reaction of acetylureas with HCHO and secondary amines in a refluxing solvent. The yield of product was increased and reaction time was reduced by refluxing the reactants in a hydrocarbon such as C6H6 and removing H2O by distillation

ACCESSION NUMBER: 1973:442003 CAPLUS
DOCUMENT NUMBER: 79:42003
TITLE: Aminomethyl derivatives of acetylureas
INVENTOR(S): Pylaeva, O. E.; Mamaev, V. P.
PATENT ASSIGNEE(S): Novosibirsk Institute of Organic Chemistry
SOURCE: U.S.S.R. From: Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1973, 50(16), 50.
CODEN: URXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Russian
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
SU 375288	T	19730323	SU 1971-1690479	19710804
PRIORITY APPLN. INFO.:			SU 1971-1690479 A	19710804

L19 ANSWER 22 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The continuous preparation of oligomers (d.p. 2-5) by formaldehyde [50-00-0] condensation with primary or secondary amines I (R1 = H, o-Me, p-CH2C6H4NH2-p; R2 = H, Me, Et) was achieved by separating the HCl-catalyzed condensation product into 1:1, 5:1, or 1:3 side stream-main stream portions, the side stream being recycled at .leq.40.deg. to be mixed with fresh catalyst and amine and the main stream being carried to final condensation at 80-200.deg.. Thus, aniline (II) [62-53-3] and HCl (2.32:1 II-HCl mole ratio) were cooled to 15.deg., condensed with CH2O (2:1 II-CH2O mole ratio), and the product equally separated into the side stream (.leq.25.deg.) and main stream. The main stream(.leq.40.deg.) was heated to 100-2.deg., treated with NaOH at 110.deg. and distilled at 100-230.deg. to give 89% oligomer mixture (d.p. = 2-4). I mixture was treated with phosgene to give polyisocyanate mixts.

ACCESSION NUMBER: 1973:136977 CAPLUS
DOCUMENT NUMBER: 78:136977
TITLE: Aromatic polyamines
INVENTOR(S): Eifler, Willi; Raue, Roderich; Rohe, Ernst Heinrich; Finkel, Josef
PATENT ASSIGNEE(S): Bayer A.-G.
SOURCE: Ger. Offen., 20 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2127263	A1	19730104	DE 1971-2127263	19710602
US 3931320	A	19760106	US 1972-256036	19720523
GB 1371960	A	19741030	GB 1972-24940	19720526
IT 958138	A	19731020	IT 1972-50592	19720530
BE 784217	A1	19721130	BE 1972-118123	19720531
NL 7207358	A	19721205	NL 1972-7358	19720531
BR 7203539	A0	19730531	BR 1972-3539	19720531
ES 403366	A1	19750416	ES 1972-403366	19720531
FR 2140224	A1	19730112	FR 1972-20008	19720602
AU 7243590	A1	19740103	AU 1972-43590	19720619
PRIORITY APPLN. INFO.:			DE 1971-2127263 A	19710602

L19 ANSWER 23 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The title compns. consist mainly of methylenedianilines in which 4-50% of the NH2 groups are substituted with C1-8 primary or secondary alkyl groups, and are prepared by condensing mixts. of N-alkylanilines and PhNH2 with HCHO in the presence of an acid or by the reductive alkylation of methylenedianilines. Thus, 210 g Tonox (I), a com. mixture containing 4,4'-methylenedianiline (II) 56, 2,4'-methylenedianiline 14, 2,2'-methylenedianiline 2, and higher functional diphenylmethane bases 28 weight %, was mixed with 14.5 g acetone, 75 ml MeOH, and 3.0 g 5% Pt sulfide/C and heated 1.75 hr at 95° and 485-900 psig H. The reaction mixture was cooled, filtered, and evaporated to give 213 g of a brown oil which solidified to a product which melted over a broadrange, becoming completely clear at 50° and in which 12.5% of the primary amino groups were alkylated to isopropylamino groups. The product (29.6 g) was melted and mixed with 100 g Epon 828, deaerated, and hardened 2 hr at 80° and 3 hr at 150° to give a molding with heat deformation temperature (ASTM D648-56) 152°. In another type of preparation, a mixture of PhNH2 167.4. iso-PrNHPh27.0, and 37% HCHO 46.9 g was heated 3 hr at 65°, separated, and the organic layer mixed with 7 ml concentrated HCl and dried by azeotropic distillationat 110° for 6 hr. The mixture was then neutralized, washed, steam distilled to remove excess amines, and the residue dried to give a brown oil, which cured Epon 828 to a heat deformation temperature of 143°. Curing agents were also prepared by reductive alkylation of I with HCHO, PrCHO, iso-BuCOMe, and 2-octanone, and of II with HCHO, acetone, MeCOEt, and iso-Bu-COMe. These compns., liqs. or low melting solids, are easily incorporated into epoxy resins.

ACCESSION NUMBER: 1970:79905 CAPLUS
DOCUMENT NUMBER: 72:79905
TITLE: Partially N-alkylated diphenylmethane bases as resin hardeners
INVENTOR(S): Sundholm, Norman K.
PATENT ASSIGNEE(S): Uniroyal, Inc.
SOURCE: Ger. Offen., 24 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1937937		19700129		
FR 2014715			FR	
GB 1273371			GB	
US 3634275		19720000	US	
ZA 6904547		19690000	ZA	
PRIORITY APPLN. INFO.:			US	19680725

L19 ANSWER 24 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB N,N-Dimethylamino alcs. are prepared by replacing each of the hydrogens of the amino group with a Me radical by treating the alc. with at least 3 moles of HCHO/mole amine. The process also includes the selective production of N,N-dialkylamino alcs. such as N,N-dimethylamino alcs. and isomers using different aldehydes, by controlling the reaction mixture to remove HCO2H prior to separation of the methylated amino alc. or to ensure the presence of HCO2H. Dialkylamino primary and secondary alcs. are converted to dialkylamino secondary and tertiary alcs, resp. Thus, Me2C(NH2)CH2OH and HCHO introduced into a bomb and rocked 4 hrs. at temps. ranging from 114-126° to 160-3° and the product dehydrated by azeotropic distillation with PhMe and fractionated gave 69.2 to 81.0% yields of Me2C(NMe2)CH2OH (I). I (109 g., 95.5%), 100 ml. H2O, 1 ml. HCO2H, and 100 ml. PhMe distilled through a column, freed from H2O, and fractionated yielded 70% Me2C(OH)CH2NMe2. EtCH(NMe2)CH2OH distilled with 3 weight % HCO2H 8 hrs. gave 44% EtCH(OH)CH2NMe2. In the production of N,N-dialkylamino alcs. by reacting an amino alc. with an aldehyde and separating the N,N-dialkylamino alc. from the mixture, the addition of a strong base to the mixture prior to the separation neutralizes the HCO2H present and thus reduces the production of isomers.

ACCESSION NUMBER: 1968:505883 CAPLUS
DOCUMENT NUMBER: 69:105883
TITLE: N,N-Dimethylamino alcohols from formaldehyde and amino alcohols
INVENTOR(S): Tindall, John B.
PATENT ASSIGNEE(S): Commercial Solvents Corp.
SOURCE: U.S., 5 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3402203	A	19680917	US 1964-412301	19641119
PRIORITY APPLN. INFO.:			US 1964-412301 A	19641119

L19 ANSWER 25 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Gaseous mixts. of an olefin, HCHO, and H2O2, such as produced by partial oxidation of hydrocarbons, preferably C3H8 and C4H10, are separated by extractive distillation with AcOH to give: (1) a gaseous overhead product containing HCHO and olefin, and (2) a bottom product consisting of a solution of H2O2 in AcOH. The dissolved H2O2 in the latter solution can then be converted to AcOOH in the presence of an acid catalyst. The extractant used may also consist of ethers, esters, cyclic acetals, and other carboxylic acids provided they are free of primary and secondary OH groups, inert to H2O2, and will dissolve at least 5% H2O2 at 70°. Thus, a mixture of 26.4 millimoles/min. C3H8 and 3.79 millimoles/min. O were reacted continuously at 468-71°, consuming 7% of the C3H8 and 62% of the O. This yielded a gaseous product in which, of the C3H8 consumed, 64% was converted to C3H6, 13% to C2H4, 6% to C oxides, 2% to H2O2, 4% to oxygenated C3 products, and 10% to liquid products, largely MeOH. H2O2 was produced at the rate of 0.2 part by weight per part C3H8 consumed. The oxidation mixture was then passed into a plate column equipped with a thermosiphon reboiler and a reflux condenser operating at 10° under a pressure of approx. 150 mm. Extractant consisting of HOAc was fed into the column head at 84 ml./hr. and the column base temperature was kept at 70°. After 1 hr., overhead product contained approx. 0.444 g. HCHO, 2 g. C3H6, 0.01 g. peroxy moiety, and 66 g. C3H8. Bottom product weighed 63.4 g. and contained 0.74 g. H2O2 and 0.03 g. HCHO, the remainder being HOAc containing 2% H2O. The latter solution was vacuum concentrated to 10% H2O2, mixed with 2% p-toluenesulfonic acid, and passed into a vacuum concentrating column at 31 mm. to yield a HOAc-H2O2-HOOAc distillate containing approx. 22% HOOAc.
ACCESSION NUMBER: 1968:495975 CAPLUS
DOCUMENT NUMBER: 69:95975
TITLE: Separation of formaldehyde from hydrogen peroxide and preparation of peracetic acid
INVENTOR(S): MacLean, Alexander F.; Hobbs, Charles C.
PATENT ASSIGNEE(S): Celanese Corp.
SOURCE: U.S., 6 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3398185	A	19680820	US 1966-571975	19660812
PRIORITY APPLN. INFO.:			US 1966-571975 A	19660812

L19 ANSWER 26 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB A mass spectrometric study of the reaction between gaseous HCHO (also HCDO and DCDO) produced by the distillation of the corresponding polyoxymethylenes and O(3P) atoms produced by NO titration of N-atoms generated with a microwave discharge in mol. N at 1.5 torr. was carried out. The reaction was studied at low concns. and low conversion of the HCHO with excess O atoms, and was 1st order with respect to O atoms and HCHO. A rate constant was obtained. Atomic H, H2O, mol. O, and CO2 were identified as reaction produced and their formation was explained by reaction O + HCHO = OH + CHO (1), as suggested by Gelb (CA 31, 20564), followed by the fast secondary reactions CHO + O = CO2 + H, CHO + OH = H2O + CO, and OH + O = O2 + H. No support for Avramenko and Lorentso's suggested primary reaction step (CA 47, 9728g) O + HCHO = CO + H2O was obtained. The activation energy for (1) is 5.5 kcal./mole.
ACCESSION NUMBER: 1967:79980 CAPLUS
DOCUMENT NUMBER: 66:79980
TITLE: Reaction of O(3P) atoms with formaldehyde
AUTHOR(S): Niki, Hiromi
CORPORATE SOURCE: Ford Motor Co., Dearborn, MI, USA
SOURCE: Journal of Chemical Physics (1966), 45(6), 2330-2
CODEN: JCPSA6; ISSN: 0021-9606
DOCUMENT TYPE: Journal
LANGUAGE: English

L19 ANSWER 27 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The reaction of HC.tplbond.CCRR1OH (I) with R2CHO under anhydrous conditions, yields first an acetylenic glycol, which on alkaline cleavage gives a ketone or aldehyde and a primary or secondary acetylenic alc. In an example, 168 g. I (R = R1 = Me), 70 g. anhydrous paraformaldehyde, 60 g. of a catalyst consisting of 12% Cu acetylide on activated C, and 200 cc. CH2(OMe)2 was charged to a rocking bomb, heated 30 hrs. at 105°, cooled, and filtered and the filtrate fractionally distilled to give 95.5% 2-methyl-3-pentyne-2,5-diol (II). II (95 g.) was cleared by heating at 175°/300 mm. with 0.5 g. K2CO3 for 5.75 hrs. to yield 71 g. yellow liquid, containing Me2CO and propargyl alc. (III), b. 116-17°. Similarly 3-methyl-1-nonyn-3-ol gave 50% 4-methyl-2-decyne-1,4-diol (IV), b0.1 112°. Cleavage of IV with K2CO3 gave anhydrous III and 2-octanone.
ACCESSION NUMBER: 1964:15976 CAPLUS
DOCUMENT NUMBER: 60:15976
ORIGINAL REFERENCE NO.: 60:2765a-c
TITLE: Acetylenic glycols
INVENTOR(S): Leeds, Morton W.; Russell, James P.; Vitcha, James F.
PATENT ASSIGNEE(S): Air Reduction Co., Inc.
SOURCE: 3 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3108140		19631022	US	19591231

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AB Heavy residues formed during the condensation of CH2O and monoolefins are converted to highly hydroxylated compds. for use as commercial solvents, antigels, plasticizers for paints and varnishes, and hydraulics. The heavy residue is treated with a low mol. weight of alc. of not more than 4 C atoms, preferably in a 10% ratio. The reaction is catalyzed by an inorg. or an organic acid or an acid salt. High purity is not required for either the alc. or the acid. One to 10% by weight of acid is usually added to the residue. The reaction may be carried out at 30 to 100° preferably from 50 to 80°. Usually the reaction is conducted batchwise in a heated flask equipped with a reflux condenser. On completion of the reaction, the products are separated and recovered by distillation, azeotropic distillation, extraction or ion exchange. In a typical example, 2 kg. residue reacted with 315 kg. methanol in 74 g. H2SO4 to give 975 g. methylal, having a primary and secondary hydroxyl index of 460 and a tertiary hydroxyl index of 380.
ACCESSION NUMBER: 1963:454292 CAPLUS
DOCUMENT NUMBER: 59:54292
ORIGINAL REFERENCE NO.: 59:9801d-e
TITLE: Hydroxy hydrocarbons from residues of the manufacture of conjugated diolefins
INVENTOR(S): Auffray, Robert; Davidson, Mircea; Jenny, Robert
PATENT ASSIGNEE(S): Institut Francais du Petrole, des Carburants et Lubrifiants
SOURCE: 14 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 1313721		19630104	FR	19600420

L19 ANSWER 29 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB The active ends of an anionic polymer of styrene (I), α-methylstyrene, or p-methylstyrene are converted to OH groups by reacting with an aldehyde, such as HCHO or AcH, or with a ketone, such as Me2CO, before neutralizing the alkali metal or organo-alkali catalyst with H2O, alc., or an acid. Thus, 8.5 ml. of a fresh catalyst solution, comprising 6.7
+ 10-4 mole Na α-methylstyrene tetramer/cc. solution in tetrahydrofuran (II), was added to 50 ml. II, which was followed by distillation of 10 g. I into the flask at 0°. The flask was maintained at 0° for about 30 min., 1 ml. of dry and degassed AcH was added and the temperature raised to ambient. The deep red color disappeared
rapidly. A few ml. of MeOH acidified with HCl was added, and the polymer was precipitated by addition of alc. and vacuum-dried at 50°. The mol. weight
of the polymer was calculated from intrinsic viscosity in toluene to be 9000.
The presence of 2.0 OH groups per mol. based on this mol. weight was determined by
a Zerewitinoff test for active H (Kohler, J. Am. Chemical Society 49, 318 (1927)).

ACCESSION NUMBER: 1963:53830 CAPLUS
DOCUMENT NUMBER: 58:53830
ORIGINAL REFERENCE NO.: 58:9252e-f
TITLE: Hydroxy-terminated aromatic vinyl polymers
PATENT ASSIGNEE(S): Polymer Corp. Ltd.
SOURCE: 5 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 909673		19621031	GB	
PRIORITY APPLN. INFO.:			CA	19600611

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AB MeOH containing 40 mg. natural U/cc. as a dispersion of UO2, having a particle
size of <3 μ diameter was placed in a quartz tube. The tube was evacuated, and was exposed to an average thermal n flux of .apprx.1012 n/sq. cm. at ambient temperature (.apprx.60°). The liquid portion contained CH2OHCH2OH equivalent to 27% of the MeOH decomposed and HCHO equivalent to 22%.
The gaseous products were H and CO, equivalent to 35% of the MeOH decomposed,
CH4 11, and minor amts. of C2H4, C2H2, and CO2. About 3.5% of the original MeOH was decomposed Similarly: AcOH was changed (2.7%) to dimethylsuccinate, showing that 10% of the decomposed AcOH was converted into succinic acid. EtOH and C6H14 produced dodecanes, butanediols, octanols, and traces of other substances. Acetonitrile was converted 15% to succinonitrile. MeOAc so treated produced CH2OHCH2OH enough to indicate 11% of the 3.4% MeOAc decomposed to glycol acetate, 9% to dimethyl succinate, and 20% Me acrylate and β-acetoxypropionate. Anisole (2.2%) converted into dimethoxybiphenyl, glycol diphenyl ether, C6H6, PhOH, and MeOH. Ac2O produced succinic anhydride from 20% of the anhydride decomposed, 35% CO2, and 15% C6H6. MeOH and H2O had 2% of the MeOH decomposed to glycol 25% and HCHO 35%. With modified apparatus 8% of MeOH
decomposed and 60% of that was converted to CH2OHCH2OH. Adding CCl4 raised the amount decomposed to 10%, with 70% of it glycol. AcOH was completely esterified with MeOH. EtOH and C6H14 produced butanediols, octanols, and dodecanes.

ACCESSION NUMBER: 1963:30935 CAPLUS
DOCUMENT NUMBER: 58:30935
ORIGINAL REFERENCE NO.: 58:5190b-e
TITLE: Nuclear fission in synthesizing organic compounds
INVENTOR(S): Conner, Willard P., Jr.; Davis, William E.
PATENT ASSIGNEE(S): Hercules Powder Co.
SOURCE: 8 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3065159		19621120	US	19571217

L19 ANSWER 31 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Deasy's (CA 53, 20872f) findings on collagen (I) dinitrophenyl (DNP) derivs. were confirmed. Partly degraded I was used. I was plumped 14 days at pH 10.0, 1 day at pH 2.0, dried at 50°, and analyzed for primary amino N by the van Slyke method modified by Deyl and Rosmus. A swelling curve of I was obtained by the Dogadkin apparatus (CA 51, 17221a). A
titration curve of I was obtained by the method of Atkin and Campos (CA 18, 3290), the determination being made after 24 hrs. of treatment as the equilibrium
was attained very slowly. I was acetylated by a freshly prepared mixture (1:1) of AcOH and Ac2O for 8 days, washed on a filter with acetone, and finally extracted with acetone 4 times in 24 hrs. in a Soxhlet apparatus Acetylated groups were determined by the difference between total and labile Ac
groups. Total Ac groups were determined by steam distillation after refluxing with 2N H2SO4. Labile acetylated groups were determined by the Blackburn-Phillips method (CA 39, 959). Dinitrophenylation of I, chromatographic separation of DNP amino acids formed and their determination were done
by the method of Levy (CA 49, 101h). The insol. residue was hydrolyzed by a known amount of 6N HCl for 12 hrs. at 100° in a sealed ampul, and the hydrolyzate was chromatographed in 2 dimensions by a mixture of chlorotoluene-EtOH-pyridine 0.8N NH4OH and by an ascending mixture of 0.5M phosphate (495 g. primary and 537 g. secondary phosphate in 3000 ml. H2O). Finally, the bound HCHO was determined by a modified Schulek method
(cf. R. and Z., CA 55, 22879b). The following results (in μmole/g.) were obtained before and after reaction with HCHO: Primary NH2 groups (Van Slyke) ε-lysine 0.34, 0.24; α-lysine + glycine + X 0.15, 0.13; stable Ac groups 0.47, 0.35; labile Ac groups 0.58, 0.59. After the DNP action: bis-DNP-lysine 0.15, 0.15; mono-DNP-lysine 0.35, 0.25; DNP-glycine 0.03, 0.03; DNP-X 0.02, 0.00. The titration curves give 0.50 and 0.37 primary amino acids. HCHO, bound on I is 0.14 μmole/g. As N-terminal residues in acid-hydrolyzed I, lysine, glycine, and X (undetd. amino acids) were found. X acids disappear after HCHO treatment at pH 2.5-3.0 at 50°. X is probably DNP-proline. α-Amino groups do not take part in the reaction with HCHO; ε-amino groups do. Therefore, CH2-ε-lysine and CH2-X bonds are formed. The increase of labile acetyl groups shows that a part of the ε-lysine groups formed a methylol derivative RNHCH(NHCOR)CH2CH2NHCH2OH. HCHO (1 mole) probably
reacts with 1 mole of lysine groups. A probable formula of degraded I after reaction with HCHO is given.

ACCESSION NUMBER: 1962:483904 CAPLUS
DOCUMENT NUMBER: 57:83904
ORIGINAL REFERENCE NO.: 57:16817h-i,16818a-e
TITLE: Characteristic cross-links during the reaction of collagen with formaldehyde in an acid medium
AUTHOR(S): Rosmus, Jan; Deyl, Zdenek
CORPORATE SOURCE: Central Res. Inst. Food Ind., Prague
SOURCE: Kozarstvi (1962), 12, 99-101
CODEN: KOZAAT; ISSN: 0023-4338
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 32 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB cf. CA 54, 19499i. The reactivity of a series of substituted phenylhydrazines towards aldehydes and ketones was investigated. Some of the hydrazines were useful for the separation of specific aldehydes from mixts.
with other carbonyl compds. The appropriate carbonyl compound (0.0025 mol) in 2.5 cc. EtOH treated with 0.00375 mol suitable hydrazine in EtOH and the product filtered off after 24 h. storage at 20° gave the corresponding hydrazone (hydrazine and carbonyl compound used, time to beginning precipitation of hydrazone, % yield, crystal form, and m.p. of hydrazone
obtained given): 2,4-Me2C6H3NHNH2 (I), CH2O (II), 40 h., 40, needles, 118° (MeOH); I, BzH (III), 15 min., 70, -, -; I, o-O2NC6H4CHO (IV), 5 min., 60, ruby-red needles, 141-2° (AcOH); I, m-O2NC6H4CHO (V), 5 s., 90, red prisms, 185-6° (AcOH); I, p-O2NC6H4CHO (VI), 5 s., 75, dark red prisms, 171-2° (AcOH); I, p-Me2NC6H4CHO (VII), 10 min., 90, leaflets, 139-41° (90% AcOH); I, PhCH:CHCHO (VIII), 60 min., 15, -, -; I, o-HOC6H4CHO (IX), 10 h., 55, -, -; I, AcPh (X), 24 h., 30, light brown needles, 89-90° (EtOH) (decomposed within a few hrs.); I, cyclohexanone (XI), -, -, -, -; 2,4-Me2C6H3NMeNH2 (XII), II -, -, -, -; XII, III, -, -, -, -; XII, IV, -, -, -, -; XII, V, 96 h., 50, gold-yellow leaflets, 90-1° (EtOH); XII, VI, 60 min., 70, orange-red needles, 97°; XII, VII, -, -, -, -; XII, VIII, -, -, -, -; XII, IX, -, -, -, -; XII, X, -, -, -, -; XII, XI, -, -, -, -; 2,4-BrMeC6H3NHNH2 (XIII), II -, -, -, -; XIII, III, 10 h., 45, -, -; XIII, IV, 10 min., 85, -, -; XIII, V, 5 mm., 60, -, -; XIII, VI, 8 min., 65, -, -; XIII, VII, 60 min., 65, prisms, 124-5° (EtOH); XIII, VIII, 5 min., 75, -, -; XIII, IX, 24 h., 55, -, -; XIII, X, 60 h., 35, needles, 64-5° (decomposed within a few hrs.); XIII, XI, -, -, -, -; 2,4-BrMeC6H3NMeNH2 (XIV), II, -, -, -, -; XIV, III, -, -, -, -; XIV, IV, 2 min., 90, gold-yellow needles, 116° (EtOH); XIV, V, 1 min., 90, gold-yellow needles, 134-5° (1:1 CHCl3-EtOH); XIV, VI, 1 min., 100, gold-yellow needles, 158° (1:1 CHCl3-EtOH); XIV, VII, 15 min., 100, pale yellow leaflets, 137-8° (1:5 CHCl3-EtOH); XIV, VIII -, -, -, -; XIV, IX, 15 min., 85, needles, 79-80° (EtOH); XIV, X, -, -, -, -; XIV, XI -, -, -, -; 4,2-BrMeC6H3NHNH2 (XV), II, -, -, -, -; XV, III, 35 min., 70, -, -; XV, IV, 10 min., 100, -, -; XV, V, 1 min., 85, -, -; XV, VI, 1 min., 90, -, -; XV, VII, 50 min., 100, pale yellow needles, 173-5° (AcOH); XV, VIII, 1 min., 80, -, -; XV, IX, 5 h., 20, -, -; XV, X, 8 h., 40, needles, 63° (EtOH) (decomposed within a few hrs.); XV, XI, -, -, -, -; 4,2-BrMeC6H3NMeNH2 (XVI), II, -, -, -, -; XVI, III, -, -, -, -; XVI, IV, 1 h., 85, orange needles, 102° (EtOH); XVI, V, 5 min., 80, gold-yellow needles, 117-18° (EtOH); XVI, VI, 3 min., 85, orange needles, 145° (1:5 CHCl3-EtOH); XVI, VII, 10 h., 90, light yellow leaflets, 95° (EtOH); XVI, VIII, -, -, -, -; XVI, IX, 2 min., 85, needles, 68-9° (EtOH); XVI, X, -, -, -, -; XVI, XI, -, -, -, -; 2,4-Br2C6H3NHNH2 (XVII), II, -, -, -, -; XVII, III, 1 min., 60, -, -; XVII, IV, 40 min., 50, -, -; XVII, V, 15 min., 45, -, -; XVII, VI, 5 min., 50, -, -; XVII, VII, 1 h., 70, prisms, 156° (AcOH); XVII, VIII, 5 s., 75, pale yellow needles, 162-3° (AcOH); XVII, IX, 15 s., 90, needles, 154-5° (AcOH); XVII, X, 3 h., 70, prisms, 86 (decomposed within a few hrs.); XVII, XI, 5 s., 60, leaflets, 60-1°; 2,4-Br2C6H3NMeNH2 (XVIII), II, -, -, -, -; XVIII, III, 5 s., 55, needles, 90-1° (MeOH); XVIII, IV, 5 s., 80, needles, 159-60° (EtOH); XVIII, V, 5 s., 80, needles, 169-70° (PrOH); XVIII, VI, 5 s., 20, needles, 190° (EtOH); XVIII, VII, 5 s., 85, prisms, 117° (MeOH); XVIII, VIII, 5 s., 85, needles, 91-2° (MeOH); XVIII, IX, 5 s., 75, needles, 88° (EtOH); XVIII, X, -, -, -, -; XVIII, XI, -, -, -, -; 4,3-BrMeC6H3NHNH2 (XIX), II, -, -, -, -; XIX, III, 10 min., 55, prisms, 126° (EtOH); XIX, IV, 30 min., 80, ruby-red prisms,

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175° (decompn.) (Ac-OH); XIX, V, 30 min. 85, orange-red prisms, 152-3° (AcOH); XIX, VI, 5 min., 100, ruby-red leaflets, 174-6° (AcOH); XIX, VII, 5 min., 75, leaflets, 161-3° (decompn.) (AcOH); XIX, VIII, 1 min., 70, yellowish leaflets, 143-4° (EtOH); XIX, IX, 4 min., 80, leaflets, 163-4° (decompn.) (AcOH); XIX, X, 4 h., 15, leaflets, 102-4° (EtOH) (decompd. within a few hrs.); XIX, XI -, -, -, -, -; 4,3-BrMeC6H3NMeNH2 (XX), II, -, -, -, -, -; XX, III, 5 s., 85, light yellow needles, 130° (EtOH); XX, IV, 5 min., 60, red needles, 131° (EtOH); XX, V, 12 min., 60, orange-red needles, 138-9° (3:1 EtOH-CHCl3); XX, VI, 2 min., 80, orange-red leaflets, 185-6° (1:1 EtOH-CHCl3); XX, VII, 24 h., 80, pale yellow needles, 146-7° (3:1 EtOH-CHCl3); XX, VIII, 5 s., 85, pale yellow needles, 143-4° (EtOH); XX, IX, 1 min., 85, pale yellow leaflets, 111° (EtOH); XX, X, -, -, -, -; XX, XI, -, -, -, -; 3,4-BrMeC6H3NHNH2 (XXI), II, -, -, -, -; XXI, III, 2 h., 35, leaflets, 119-21° (50% EtOH); XXI, IV, 5 min., 85, red prisms, 167-8° (AcOH); XXI, V, 5 min., 85, orange prisms, 146-8° (EtOH); XXI, VI, 20 min. 60, red-brown needles, 150-1° (EtOH); XXI, VII, 1 min., 95, pale yellow prisms, 189-90° (1:1 EtOH-AcOH); XXI, VIII, 1 min., 65, pale yellow prisms, 128° (25% EtOH); XXI, IX, 5 min., 80, needles, 166° (25% EtOH); XXI, X, 45 min., 65, leaflets, 82-4° (EtOH) (decompd. within a few hrs.); 3,4-BrMe-C6H3NMeNH2 (XXII), II, -, -, -, -, -; XXII, III, 5 s., 65, leaflets, 89-90° (EtOH); XXII, IV, 1 min., 60, orange needles, 138-9° (1:3 CHCl3-EtOH); XXII, V, 10 min., 80, red leaflets, 133-4° (1:3 CHCl3-EtOH); XXII, VI, 30 s., 70, orange needles, 178° (1:3 CHCl3-EtOH); XXII, VII, 2.5 h., 60, pale yellow needles, 147° (1:3 CHCl3-EtOH); XXII, VIII, 30 s., 75, pale yellow leaflets, 99-100° (1:3 CHCl3-EtOH); XXII, IX, 30 s., 90, leaflets, 119° (1:3 CHCl3-EtOH); XXII, X, -, -, -, -, -; XXII, XI, -, -, -, -.VI (375 mg.) and 305 mg. IX in 7 cc. EtOH treated with 600 mg. XII in 3 cc. EtOH and kept 24 h. at room temp. yielded 480 mg. deriv. of VI. α,2,4-Trimethylphenylhydrazone (280 mg.) of VI in 2.5 cc. concd. H2SO4 kept 1.5 h. at room temp., poured into 50 cc. iced H2O, and filtered after several hrs. gave 97 mg. VI, m. 106°. IX (305 mg.) and 250 mg. XI in 5 cc. EtOH treated with 800 mg. XXII in 3 cc. EtOH and filtered after 8-10 h. gave 640 mg. deriv. of IX. 3-Bromo-α,4-dimethylphenylhydrazone (640 mg.) of IX in 10 cc. EtOH and 10 cc. concd. HCl refluxed 0.5 h., cooled, dild. with H2O, steam distd., and the distillate extd. with Et2O gave 170 mg. IX.

ACCESSION NUMBER: 1962:73214 CAPLUS
DOCUMENT NUMBER: 56:73214
ORIGINAL REFERENCE NO.: 56:14125h-i,14126a-i,14127a-c
TITLE: Condensation of carbonyl compounds with hydrazines. V. The reaction of aldehydes and ketones with disubstituted phenylhydrazines and their α-methyl derivatives
AUTHOR(S): Stroh, Hans Hartwig; Nikolajewski, Hans Edmund
CORPORATE SOURCE: Humboldt Univ., Berlin
SOURCE: Chemische Berichte (1962), 95, 562-70
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 56:73214

L19 ANSWER 33 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The addition reactions of d-limonene (I) with HCHO (II), MeCHO, EtCHO, and R2NH as well as the preparation of limonenylcarbinol derivs. were described. A mixture of 20 g. I, 4.5 g. II, and 10 g. EtOH was sealed in a glass tube and heated at 200-20° for 12 hrs. to give 2.8 g. (11%) limonenylcarbinol (III), b4 102-5°, d8 0.9612, n12D 1.5069, phenylurethan m. 54-5°. I (45.3 g.), 10 g. II and 20 g. Ac2O at 180-90° for 5 hrs. in an autoclave gave 29.6% limonenylmethyl acetate (IV), b4 96-106°, d28 0.9618, n28D 1.4790. Saponification of IV (13 g.) with 6 g. KOH at 180° 4 hrs. gave 96% 1,8(9)-p-menthadien-10-ylcarbinol (V), b4 102-6°, d17, 0.9603, n17D 1.5020; phenylurethan m. 56-7°. Reduction of 3.93 g. V in MeOH with Pd-BaSO4 containing 3% Pd gave 3 g. 1-p-menthen-10-ylcarbinol (VI), b4.5 100-3°, n13D 1.4923. To a cooled mixture (-5°) of 12 g. 1-p-menthene, 3 g. II, 17 g. 95% AcOH, and 4 g. Et2O a mixture of 7 g. 95% AcOH and 2.5 g. 98% H2SO4 was added, stirred for 5 hrs. after standing at room temperature overnight, extracted with Et2O to give 3 g. 1(2)-p-menthen-6-ylmethyl acetate (VII), b4 90-100°, n6D 1.4860. Saponification of VII with KOH gave the corresponding carbinol, b3 95-7°, n9D 1.4896. II and III heated at 150-70° for 6 hrs. gave formaldehyde mono-1,8(9)-p-menthadien-10-yl acetal (VIII), b5 155-162°, n20.5D 1.5066, d20.5 1.306. The esters of III with maleic, phthalic, and succinic acids were prepared. Employing palmitoyl, caprylyol, isovaleryl, phenylacetyl, and cinnamoyl chloride, III gave esters of the corresponding acids. To a mixture of 4 g. CrO3, 5 ml. H2O, and 100 ml. AcOH, a mixture of 9 g. III, 30 ml. Me2CO, and 20 ml. AcOH was added in 25 min. at 50-5° with stirring, after 4.5 hrs. the mixture poured into H2O, extracted with Et2O, and fractionally distilled to give 3.5 g. 3-(4-methyl-3-cyclohexen-1-yl)-3-buten-1-al (IX), b4 88° n8D 1.5045; 2,4-dinitrophenylhydrazone (DNP) m. above 220°; semicarbazone m. 192°. III (5 g.) with 18.5 g. Al[OCH(Me)2]3 in 150 g. Me2CO and 150 g. anhydrous C6H6 refluxed for 40 hrs. gave 1 g. 6-(4-methyl-3-cyclohexen-1-yl)-3,5-heptadien-2-one (X), b3 125-33°, n10D 1.5271, λ 295 mμ, ε 4480, λ 223 mμ, ε 3340; DNP m. 179-80°, pos. iodoform reaction. Similarly, III and MeCOEt gave 7-(4-methyl-3-cyclohexen-1-yl)-4,6-octadien-3-one (XI), b2 125-132°, n23D 1.4806, λ 291 mμ, ε 6650, λ 225 mμ, ε 4340, neg. iodoform reaction; DNP m. 203°. Me, Et, PhCH2, and allyl ethers of III were prepared and their b.p., nD, d24, % yield given: Me, b12 85-6°, 1.4870, 0.9317, 80; Et, b4 96-7°, 1.4921, 0.9353, 90; allyl, b17 115-18°, 1.4927, 0.9293, 80; PhCH2, b10 175-9°, 1.5300, 0.9885, 90. I (34 g.), 1.5 g. EtCHO, and 1 g. ZnCl2 gave 6-propylidene-1,8(9)-p-menthadiene, b3 130-6°, n17D 1.5130, d17 0.9200, λ 224 mμ, ε 4220, while the treatment in AcOH with a catalytic amount of H2SO4 gave cyclic ether, b0.5 110-14°, n16D 1.4970, d16 0.9734. A mixture of 25 g. Me2NH, 34 g. I, and 5.8 g. II in 60 g. AcOH was refluxed 16 hrs. to give 11% N,N-dimethyllimonenylmethylamine (XIII), b3.5 92-3°, which reacted with Wagner's reagent to give adduct of K4Fe(CN)6. Similarly, Et2NH gave 5% N,N-di-Et derivative of XIII, b3 101°.

ACCESSION NUMBER: 1961:112238 CAPLUS
DOCUMENT NUMBER: 55:112238
ORIGINAL REFERENCE NO.: 55:21159c-i
TITLE: Reaction of limonene with aldehydes
AUTHOR(S): Suga, Kyoichi; Watanabe, Shoji
SOURCE: Kogakubu Kenkyu Hokoku (Chiba Daigaku) (1960), 11(No. 19), 63-77
CODEN: CDKKAN; ISSN: 0577-6848
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 34 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB A reversible function resin, which reversibly takes up or gives up small organic mols., depending on their functional group, was prepared Cross-linked poly(methacryloylhydrazine) was obtained by treating methyl methacrylate-divinylbenzene copolymer with aqueous 80% solution of hydrazine. HCHO easily condenses with the resin at 100° and can be taken out by steam distillation in an acidic condition. The optimum content of hydrazine in the resin was 10 cc./g. resin in order to obtain the maximum degree of condensation with HCHO. The amount of HCHO taken up by the resin was 28.3 mg./g. resin when the concentration of HCHO was 9.25% (condensed at 100°, 3 hrs.). This amount was nearly proportional to the HCHO concentration. The condensation was usually accompanied with secondary reactions at higher temps. The analysis of the resin for N content by Dumas' method shows only 1.8%; the N content estimated from the amount of bound HCHO was 3%, indicating that some of hydrazine groups were linked to more than 1 HCHO.

ACCESSION NUMBER: 1961:15756 CAPLUS
DOCUMENT NUMBER: 55:15756
ORIGINAL REFERENCE NO.: 55:3105h-i,3106a-b
TITLE: Reversible function resins. I. Preparation and properties of cross-linked poly(methacryloylhydrazine)
AUTHOR(S): Sugihara, Mizuho; Okamoto, Nagahisa
SOURCE: Kagaku to Kogyo (Osaka, Japan) (1959), 33, 343-8
CODEN: KKGOAG; ISSN: 0368-5918
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 35 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Irradiation of 5.56 millimoles D-mannose (III) in 100 ml. H2O with a Co60 source to a total energy input of 6.65 + 1022 e.v. gave mannonic (IV) and mannuronic (V) acids and their δ- and δ-lactones, II, and erythrose (VI). The products were identified by paper chromatography with 4:1:5 BuOH-AcOH-H2O. Similar conclusions were derived from autoradiographs of paper chromatograms of irradiated solns. of mannose-1-C14. The distillate from irradiated solution contained HCO2H. The extent of formation of acids and H2O2 and changes in the ultraviolet spectrum were measured as a function of energy input during the irradiation. Isotope-dilution analysis was used to estimate the products
obtained on irradiation of 5.56 millimoles III in 100 ml. H2O in the presence of O and at a dose rate of 1.60 + 1017 e.v./ml. sec. for 39 hrs.; yields at total energy inputs of 3.7 + 1022 and 2.25 + 1023 e.v., resp., were: III, 3.5, 0.16; II, 0.44, 0.26; D-xylose (VII), 0.06, 0.17; glyoxal, 0.40, 1.40; (HOCH2)2CO, 0.05, 0.31; H2C2O4, 0.04, 0.74; HCHO, 0.18, 0.18; sugar acids and VI (estimated from paper chromatography), 0.46, 0.57, and 0.12, 0.69, resp.; CO2 (determined gravimetrically), 0.03, 2.33; and HCO2H (estimated by titration of the volatile acid), 0.22, 0.34 millimoles. Initial G-values were: for consumption of III, 3.5; and for formation of II, 0.5; H2CO, 0.3; glyoxal, 0.64; sugar acids, 1.6; and VI, 0.18. Expts. with D-mannose-1-C14 indicated that the primary degradation processes included (a) oxidation to IV
and V, (b) direct scission of the 1,2-bond to form II and H2CO, (c) scission of the 2,3-bond to give 2-carbon fragments and VI, and (d) scission of the hexose to give 3 two-carbon fragments. Secondary processes led to formation of II (from IV), VII (from V), H2C2O4, HCO2H, and CO2.

ACCESSION NUMBER: 1961:11669 CAPLUS
DOCUMENT NUMBER: 55:11669
ORIGINAL REFERENCE NO.: 55:2252a-e
TITLE: Radiation chemistry of carbohydrates. VI. Action of γ-radiation on aqueous solutions of D-mannose in oxygen
AUTHOR(S): Phillips, G. O.; Criddle, W. J.
CORPORATE SOURCE: Univ. Coll., Cardiff, UK
SOURCE: Journal of the Chemical Society, Abstracts (1960) 3404-12
CODEN: JCSAAZ; ISSN: 0590-9791
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB The effect of variations in reaction conditions on the nature and amount of the end products in the telomerization of styrene with HCHO in AcOH catalyzed by concentrated H2SO4 was examined 4-Phenyl-1,3-dioxane and 1-phenyl-1,3-propanediol diacetate were isolated by fractional distillation and the average mol. weight of the total product measured by the
f.p. depression method in benzene. The average mol. weight of the total product
was a function of the formaldehyde-styrene ratio when the catalyst concentration was constant The degree of polymerization was an almost
linear function of the catalyst concentration A relatively large amount of 4-phenyl-1,3-dioxane is formed in the 1st few min., together with the normal telomerization products. This cyclic formal was split by protolysis in a comparatively slow secondary reaction with styrene; it thus acted as an intermediate formaldehyde donor. A carbonium ion mechanism was suggested for the reaction.

ACCESSION NUMBER: 1960:103458 CAPLUS
DOCUMENT NUMBER: 54:103458
ORIGINAL REFERENCE NO.: 54:19688g-i
TITLE: Telomerization and Prins reaction of styrene and formaldehyde in acetic acid. Role of cyclic formal in the reaction mechanism
AUTHOR(S): Heslinga, A.
CORPORATE SOURCE: Plastics Research Inst. T. N. O., Delft, Neth.
SOURCE: Recueil des Travaux Chimiques des Pays-Bas et de la Belgique (1960), 79, 222-30
CODEN: RTCPB4; ISSN: 0370-7539
DOCUMENT TYPE: Journal
LANGUAGE: English

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GI For diagram(s), see printed CA Issue.
AB The base-catalyzed formation of aldols from Me2CO and CH2O according to Tollens, as well as the closely connected crossed Cannizzaro reaction was demonstrated by paper chromatographic investigations. To a solution of 4 ml.
Me2CO in 41 ml. 35% formalin was added a solution of 4 g. NaOH in 20 ml. H2O at 0°. Samples were taken after 0.09, 0.25, 0.5, 1, 2, 3, 18, 24, 42, 48, and 96 hrs., resp., acidified with 2N HCl, 0.003 ml. applied to Whatman Number 1 paper [together with CH2.CR1R2.CO.CR3R4.CH2.O (I, R1 = R2 = R3 = R4 = CH2OH) (Ia) (anhydroenneaheptose) and 3-oxobutanol as test compds.], chromatographed (descending) with 6:2:7 BuOH-MeOH-H2O and developed with Tollens reagent. Ia was found to be one of the main products in the mixture The degradation of perhydroxymethylated carbonyl systems (e.g. Ia) by inorg. and organic bases as well as by acids, came to a standstill after cleaving one or a maximum of 2 mols. CH2O. To 0.5 g. Ia in 5 ml. H2O was added 5 ml. 5N NaOH at 20°; after 2, 15, 30 and 60 min., resp., samples were chromatographed without or with previous acidification. Aided by the relationship of the RM values with the number of
OH groups, the degradation products were found to be I (R1 = R2 = R3 = CH2OH, R4 = H), I (R1 = R3 = CH2OH, R2 = R4 = H), I (R1 = R2 = CH2OH, R3 = R4 = H), and (HOCH2)3CCOC(CH2OH)3. It was demonstrated, that the degradation in the presence of acceptors such as salicylamide, p-aminobenzoic acid, anthranilic acid, β-naphthol, and acetoacetate, stopped at the same dealdolization stages. This limited reversibility of the aldol formation of carbonyl compds. by CH2O was explained by an anionotropic effect, which, in presence of Lewis acids, predominated the secondary reaction scheme of the base- and acid-catalyzed aldol reaction and therefore also of the Mannich reaction. This effect was responsible for the nucleophilic exchange of aldol hydroxyls by amine residues under formation of Mannich bases, when the degradation was carried out with organic bases. To 15 g. Ia in 200 ml. H2O was added 72 ml. piperidine (II), the mixture extracted with Et2O, and the extract dried and distilled to give 33 ml. dipiperidinomethane, b15 103-4°.
After standing 5 days, the aqueous phase yielded 8 g. 1,1,3,3-tetrakis(piperidinomethyl)acetone (III), m. 112-13° (AcOH), infrared spectrum given. A solution of 5 g. Ia in 25 ml. II was refluxed 1 hr., concentrated in vacuo, and AcOH added to the oil to give 3.5 g. I (R1 = R2
= CH2OH, R3 = CH2NC5H10, R4 = H), m. 107-8°, infrared spectrum given. The tribenzoate of I (R1 = R2 = R3 = CH2OH, R4 = H), m. 172-3°. Ia (6 g.) in 25 ml. II refluxed 7 hrs. yielded 4 g. I (R1 = R3 = CH2NC5H10, R2 = R4 = H), m. 94-5° (AcOEt), infrared spectrum given. I ((1 g.), R1 = R2 = CH2OH, R3 = CH2NC5H10, R4 = H), refluxed 6 hrs. with 6 ml II gave I (R1 = R3 = CH2NC5H10, R2 = R3 = H). Heating 0.5 g. I (R1 = R2 = CH2OH, R3 = CH2NC5H10, R4 = H), with 5 ml. H2O and 1 ml. II gave III. III was also obtained by heating 0.2 g. I (R1 = R3 = CH2NC5H10, R2 = R4 = H), with 5 ml. H2O and 1 ml. II. The acid-catalyzed aldol reaction is based on an unknown autocatalysis effect and is explained by an electrophilic addition of CH2O (in the form of the hydroxy-carbonium cation .sym.CH2OH) to the polarized enol double bond. The product formation was demonstrated on the system levulinic acid and CH2O by paper chromatographic techniques and involved compds. such as 3,5,5-tris(hydroxymethyl)dihydrodeoxypatulinic acid lactone (IV) diacetate and the dihydroxymethylene ether of IV. Levulinic acid (V) (1.2 g.), 5 ml. AcOH, 0.36 ml. concentrated H2SO4, and paraformaldehyde (VI) were refluxed
10 min. (molar ratios V/VI 1:1, 1:2, 1:3, 1:5), 0.7 g. Na2CO3 in 10 ml. H2O was added to each solution, the neutralized solns. applied to 2 Whatman

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filter papers, chromatographed (ascending), one paper sprayed with Tollens reagent and the other one with H2NOH-FeCl3. Considerable resistance was encountered with the reverse process, the solvolytic cleavage of CH2O from perhydroxymethylated carbonyl compds. by AcOH-H2SO4 and other strong mineral acids. IV (10 g.) in 50 ml. 50% H2SO4 was boiled 3 hrs., 180 ml. H2O added, the mixt. extd. with CHCl3, and the aq. layer extd. with Et2O to give 0.3 g. IV dihydroxymethylene ether, m. 160-2° (EtOH). Unchanged IV (1 g.) was recovered from the aq. layer. The Mannich reaction was believed to be a secondary stabilization reaction to the base- and acid-catalyzed aldol reaction, according to exptl. conditions. The anionotropic effect explained the fact that in the Mannich reaction (of compds. with several acidic H atoms at the same C atom), one acidic H atom cannot be substituted by the aminomethyl residue but only by a hydroxymethyl group. A special case is presented by carbonyl systems which have only one acidic H atom. Iso-PrCHO (3.6 g.), 6 g. II.HCl and 1 g. VI were refluxed 15 min. with 5 ml. abs. EtOH, 20 ml. H2O added, the pH adjusted to 1 with 2N HCl, extd. with Et2O, the Et2O evapd., and the residue taken up in MeOH and chromatographed. The chromatogram, sprayed with Tollens reagent, showed the presence of dimeric formisobutyraldol (VII). VII was also obtained by refluxing 2 hrs. 7.2 g. iso-PrCHO, 12 g. II.HCl, and 12 ml. formalin.

ACCESSION NUMBER: 1960:67833 CAPLUS
DOCUMENT NUMBER: 54:67833
ORIGINAL REFERENCE NO.: 54:12987g-i,12988a-i
TITLE: Aldol reactions of formaldehyde and its reversibility. Comparative studies of the mechanism of the Tollens reaction, the Mannich reaction, and the acid-catalyzed aldol reaction of formaldehyde
AUTHOR(S): Olsen, Sigurd; Henriksen, Arne; Brauer, Roar
CORPORATE SOURCE: Univ. Blindern-Oslo, Norway
SOURCE: Ann. (1959), 628, 1-36
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Reaction of 2,6-dimethylol-p-cresol(I)with aromatic primary amines resulted in the formation of 5,2,3-Me(HO)(HOCH2)C6H2NR'C6H4R (II). Nitroso compds. (III) were obtained upon nitrosation of II, indicating that II were secondary amines. 3-Arylbenzoxazines(IV)were prepared by reaction of II with HCHO. In the same manner N-(4-hydroxybenzyl)arylamines (V) and their nitroso compds. (VI) were obtained from 4-methylolphenol (VII). Twenty-six new compds., and 2 compds. obtained by 2 new methods were prepared and studied. I and VII were synthesized by known methods, m. 129.0° and 120.0°, resp.
II were prepared by the following general method. I (33.6 g.), 24.6 g. p-anisidine, and 30 ml. alc. containing 1.2 g. KOH refluxed 8 hrs., the mixture
cooled, neutralized with AcOH, unreacted p-anisidine removed by steam distillation, and the resulting solid dissolved in C6H6, and allowed to stand 1 day gave a white solid, and crystallization gave 6.3 g. II (R' = H and R = p-MeO). This compound (2.5 g.) in dilute HCl treated below 5° with 0.6 g. NaNO2, a reddish resinous product was obtained, this dissolved in Et2O, neutralized with dilute Na2CO3, washed with H2O, and evaporation at room temperature
gave a light reddish-brown crystalline solid, as the corresponding III. The following II and III were obtained (group on phenyl radical attached to the N of II, reaction time in hrs., % yield, m.p., solvent of crystallization,
group in III, reaction time for III, % yield, m.p., and solvent of crystallization
given): p-MeO, 8, 11.6, 120°, C6H6-ligroine, p-MeO, 2, 36.2, 93° MeOH; p-Cl, 10, 10.1, 106°, ethylene dichloride-ligroine, p-Cl, 3, 30.0, 131° MeOH; p-Me, 8, 8.2, 119°, p-Me, 3, 27, 101°, MeOH; p-Br, 9, 23.0, 109.5°, C2H4Cl2C6H6, p-Br, 4, 9.2, 135, MeOH; H, 2, 0.92, 83°, ligroine, H, 3, 29.7, 73°, MeOH-H2O; o-MeO, 16.4, 109°, alc.-H2O, -, -, -, -; p-EtO, 8, 10.4, 115.9°, alc., p-EtO, 24, 59, 101.3°, alc.-H2O. II (R = p-MeO, R' = H) (3 g.) in 50 ml. MeOH refluxed 2 hrs. with 1.6 ml. 37% HCHO, H2O added, the solution cooled to room temperature, the solid collected, and
recrystd. gave 3,4-dihydro-3-p-anisyl-6-methyl-8-methylol-1,3,2H-benzoxazine (IV, aryl = 3-p-anisyl). The following IV were obtained (3-aryl, reaction time in hrs., % yield, m.p., and solvent of crystallization
given): p-MeOC6H4, 2, 32, 108°, MeOH; p-ClC6H4, 2, 35, 107°, Me2CO-H2O; p-MeC6H4, 2, 31.8, 83°, MeOH-H2O; p-BrC6H4, 2, 48.2, 108.5°, MeOH; p-EtOC6H4, 0.5, 96.5, 94.3°, C6H6-ligroine. V were prepared in essentially the same way as were II except that 0.1 mole VII and 0.1 mole of aromatic primary amine were used. The following V (p-HOC6H4CH2NHC6H4R-p) were thus obtained (R, time in hrs., % yield, m.p., and solvent for recrystn. given): Br, 10, 19, 86.4°, ligroine-C6H6; Cl, 10, 18.0, 70.5°, ligroine-C6H6; Me, 10, 21, 90°, ligroine-C6H6, 3:1; MeO, 10, 57, 111.1°, ligroine-C6H6, 4:1; EtO, 8, 16.0, 97.4°, ligroine-C6H6, 3:1. VI were prepared in essentially the same manner, except that 3.5 g. of V was used. The following VI [p-HOC6H4CH2N(NO)C6H4R-p] were obtained (R, time in hrs., % yield, m.p., and solvent of crystallization given): p-Br, 5, 77, 131.4°, 1:1 C6H6-ligroine; p-Cl, 4, 81, 118.6°, 1:2 ligroine-C6H6; p-Me, 3, 59, 110.6°, 2:1 ligroine-C6H6; p-MeO, 4, 88, 118.8°, 4:1 ligroine-C6H6; p-EtO, 12, 53, 98.8°, 2:1 ligroine-C6H6.

ACCESSION NUMBER: 1959:121656 CAPLUS
DOCUMENT NUMBER: 53:121656
ORIGINAL REFERENCE NO.: 53:21734f-i,21735a-d

L19 ANSWER 38 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

TITLE: Synthetic products from methylolphenols, formaldehyde, and primary aromatic amines
AUTHOR(S): Noda, Miyoshi; Shimaoka, Hiroshi; Nagase, Susumu
CORPORATE SOURCE: Matsushita Elec. Works, Ltd., Osaka Prefecture
SOURCE: Journal of Organic Chemistry (1959), 24, 512-15
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Condensation of CF3 with piperidine, morpholine, and iso-Bu2NH hydroxymethyl derivs. produced the hydrates of CF3C(OH)2CH(CH2NR2)2 where NR2 = C5H10N (I), OC4H8N (II), and iso-Bu2N (III). CF3CH(OH)CH2CH2NC5H10 (IV) was prepared by NaBH4 reduction of CF3COCH2CONC5H10 (V) to CF3CH(OH)CH2CONC5H10 (VI) followed by LiAlH4 reduction. Condensation of piperidine and HCHO with EtCOCF3, BuCOCF3, and V gave the expected Mannich bases, CF3COCHRCH2NC5H10.H2O (VII). Piperidine (8.5 g.) in 17 ml. H2O and 8.5 ml. cold 37% aqueous HCHO kept 1 hr. at 0°, the mixture treated (Cellusolve-Dry Ice bath) with 11 g. CF3, the reaction flask fitted with a Dry Ice reflux condenser, the mixture brought to room temperature in 30 min., and
the precipitate recrystd. (Me2CO) yielded 48% I, m. 93-5°, containing 2 active
H atoms/mole and giving an ester by the Schotten-Baumann procedure. II, m. 83.5-7.0° (MeCOEt), and III, m. 79-81° (Me2CO), were similarly prepared in 36 and 20% yields. CF3COCH2CO2Et (184 g.) in 200 ml. boiling dry xylene treated dropwise in an apparatus according to Kibler and Weissberger [Organic Syntheses, Collective Volume III, 108(1955)] with 76.5 g.
dry C5H10NH, the mixture refluxed 30 min., concentrated in vacuo, and fractionated
gave 147 g. oily V, b7 119-20°, n27D 1.4647, m. 27.4-30.0° (corrected) (petr. ether); 2,4-dinitrophenylhydrazone m. 114.5-15.5° (corrected) (dilute MeOH); Cu chelate m. 207.0-7.5° (corrected) (dilute MeOH). V
(44.6 g.) in 200 ml. Et2O stirred at 0° with portionwise addition of 4 g. NaBH4, the mixture stirred 1.5 hrs. at room temperature, the filtered solution
stirred 1.5 hrs. at room temperature with 20 ml. 5% HCl, the filtered organic layer
washed, dried, and concentrated yielded 79% VI, m. 109.4-9.8° (corrected) (C6H6-petr. ether). VI (31.5 g.) in 100 ml. dry tetrahydrofuran and 8.7 g. LiAlH4 in 200 ml. Et2O processed according to Micovi.acte.c and Mihailovi.acte.c (C.A. 48, 10020g) and the product fractionated gave 19 g. IV, b14 94°, n24D 1.4232, d24 1.151; phenylurethan, m. 93.0-3.6° (petr. ether); p-MeC6H4SO2Me derivative m. 122.8-4.0° (EtOAc-MeOH); p-O2NC6H4CO2H.HCl derivative m. 191-3° (Me2CO-MeOH), converted by hydrogenation with PtO2 and neutralization with concentrated NH4OH
to the corresponding p-H2NC6H4CO2H derivative, m. 103.0-3.8° (corrected). An alternative method of preparing VI was investigated. CF3COCH2CO2Et (49 g.) in 50 ml. Et2O treated with 3.8 g. NaBH4 and the product fractionated gave 34 g. known CF3CH(OH)CH2CO2Et (VIII), b14.5 80-3°, n25D 1.3732; phenylurethan, m. 67-9°. VIII (49.5 g.) in 75 ml. dry xylene refluxed 2 hrs. with 27 g. dry C5H10NH, the decolorized (Nuchar) solution concentrated in vacuo, the residue extracted with water and the insol.
fraction recrystd. (C6H6) to yield 3.6 g. VI, the aqueous extract washed with
C6H6, evaporated in vacuo, and dried by azeotropic distillation with C6H6 gave 12 g. piperidinium β-hydroxy-γ,γ,γ-trifluorobutyrate, m. 100.8-1.8° (corrected) (C6H6), also produced by treating CF3CH(OH)CH2CO2H with C5H10NH. Unlike V, N-(acetoacetyl)piperidine (IX) was reduced successfully to 4-piperidino-2-butanol (X) with LiAlH4. AcCH2CO2H (65 g.) in 70 ml. xylene at 145° treated portionwise with 34 g. C5H10NH, the mixture heated 45 min., and fractionated gave 55 g. IX, b4 126-8°. IX (59 g.) in 50 ml. dry Et2O was reduced (N atmospheric) with 25 g. LiAlH4 in 500 ml.

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dry Et2O according to the method of Uffer and Schlittler (C.A. 43, 121g) to give 25 g. X, b4 103°; HCl salt m. 145° (alc.-Me2CO); benzoate-HCl m. 192° (Me2CO). EtCOCF3 (12.6 g.) treated at 0° with 8.5 g. C5H10NH and 10 ml. 37% aq. HCHO, the mixt. dild. with water, and chilled yielded 87% VII (R = Me) (XI), m. 98-100° (dil. alc.); picrate m. 105-7° (dil. MeOH). Similarly were prepd. VII (R = C3H7) (XII), m. 82-4° (picrate, m. 93-5°), and VII (R = CONC5H10) (XIII), m. 96-8° (picrate, m. 92-3°), in 85 and 90% yields. An attempt to recrystallize XIII from hot dil. MeOH caused its decompn. to N-(α-trifluoroacetylacryloyl)piperidine hydrate (XIV). V (5 g.) in 15 ml. MeOH contg. 10 drops of 15% NaOH treated dropwise at 20° with 3 g. 30% HCHO with vigorous shaking, the mixt. shaken vigorously 5 min. at 50°, treated with 5 ml. H2O, and cooled gave 4 g. XIV, m. 138.4-40.0° (dil. MeOH). XI (5 g.) in 100 ml. Et2O treated portionwise with 0.38 g. NaBH4, the mixt. stirred 1.5 hrs., the filtered soln. stirred vigorously 1 hr. with 2 g. NaOH in 50 ml. H2O, the aq. layer extd. with Et2O, and the combined dried (MgSO4) Et2O solns. distd. yielded 50% 1,1,1-trifluoro-3-piperidinomethyl-2-butanol, b4 79-81°; p-nitrobenzoate HCl salt m. 206-8° (cor.) (CHCl-Et2O). Similarly, 10 g. XII was reduced to 47% 1,1,1-trifluoro-3-piperidinomethyl-2-hexanol (XV), b4 92-5°; p-aminobenzoate HCl salt (XVI) m. 223-5°. Repeated attempts to purify the p-nitrobenzoate HCl salt (XVII) of XV by recrystn. from alc. failed. XVII (7 g.) in 100 ml. alc. hydrogenated with 150 mg. prereduced PtO2, the filtered soln. evapd., the residue neutralized with NaOH, and the brown soln. dild. with H2O yielded 63% XV p-aminobenzoate, m. 92-4°.

ACCESSION NUMBER: 1959:51161 CAPLUS
DOCUMENT NUMBER: 53:51161
ORIGINAL REFERENCE NO.: 53:9225i,9226a-i,9227a
TITLE: Condensation of some trifluoromethyl ketones with secondary amines and formaldehyde
AUTHOR(S): Grillot, G. F.; Aftergut, Siegfried; Marmor, Solomon; Carrock, Fred
CORPORATE SOURCE: Univ. of Syracuse, Syracuse, NY
SOURCE: Journal of Organic Chemistry (1958), 23, 366-9
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB cf. C.A. 51, 2791h. The initial step in condensation of >CHCR:CH- with HCHO is assumed to be an electrophilic attack of HOCH2OH2+ at the terminal C atom to give >CHCR(OH)CH(CH2OH)-. At higher acid concns. with excess HCHO dehydration may take place with formation of >C:RCCH(CH2OH)-. Theoretically these procedures may continue until all H atoms at the terminal C atoms are substituted by CH2OH groups and m-dioxane or tetrahydropyran rings may form from pairs of HO groups under the influence of acid. In addition the original condensation may be reversed by cleavage (cf. Zimmerman and English, C.A. 48, 11321c). These postulated reactions were studied by condensation of HCHO with PhMeC:CH2 (I) and PhCH:CH2 (II). HCHO (514 g., 35%), 120 g. H2SO4 and 180 g. (HCHO)n at 90° stirred 1 hr. with addition of 236 g. I and the mixture stirred 2 hrs. at 90°, diluted with C6H6 and the solution washed to neutrality, the dried solution evaporated, and the product (466 g.) distilled quickly at 3 mm., the main fractions (322 g.) fractionated at 3 mm. and the product recrystd. gave 24 g. 4-methyl-4-phenyl-m-dioxane (III), m. 39° (petr. ether) (C.A. 45, 9502d), 61 g. compound, C13H16O3 (IV), m. 125.3-5.7° (alc.), and a compound, C14H18O4 (V), m. 87.5-7.7°. The mother liquors and intermediate fractions (195.5 g.) treated with the calculated amount of H3BO3 gave 121 g. nonalc. components (VI) and 72.5 g. boric ester, hydrolyzed by stirring with 10% aqueous Na2CO3 on a steam bath, working up and fractionating to give 61 g. practically pure alc. component, C12H16O3 (VII), converted to the 3,5-dinitrobenzoate, m. 120.0-1.0°, and recovered by 1 hr. hydrolysis of 13.0 g. salt with 13 g. Na2CO3 in 800 ml. 1:3 H2O-alc. to yield 6.74 g. VII, b2.5 155°, n20D 1.5417, d20 1.1676. VI fractionated at 0.1 mm. through a 16-plate Vigreux column with 1:10 reflux ratio yielded 12 g. III, 3 g. IV, and 16 g. V. The same reaction was carried out at lower acid concentration and a smaller excess of HCHO. I (472 g.), 684 g. 35% HCHO, 80 g. (HCHO)n stirred with 160 g. H2SO4 at 90° (external cooling) and stirring continued 3.5 hrs. at 90°, the product worked up and distilled to give 11 g. crude I, 230 g. high-boiling and undistillable material, the group of fractions, b. 99-115°, repeatedly crystallized (alc. and petr. ether) and the mother liquor worked up gave altogether 53.9 g. pure compound, C11H12O (VIII), m. 62.0-2.5°. The remaining fractions separated by fractionation, H3BO3 separation and recrystn. gave 72 g. III, 52 g. IV, 1 g. V, and 67 g. VII. VIII (11.2 g.) in 35 ml. alc. hydrogenated 10 hrs. at 20° with 100 mg. PtO2 and the filtered solution evaporated gave a nearly quant. yield of 4-phenyltetrahydropyran, m. 46.0-7.0°. VIII, λ 245 mμ (log ε 4.142), is accordingly the known 4-phenyl-5,6-dihydro-1,2-pyran (cf. Borsche and Thiele, C.A. 18, 688) formed by a secondary reaction with HCHO via the intermediate H2C:CPhCH2CH2OH followed by cyclization and dehydration, a reaction similar to piperidine ring formation from I observed by Schmidle and Mansfield (C.A. 50, 13029f). VIII (11 g.) and 52 g. 35% HCHO stirred 4 hrs. at 90° with 12 g. H2SO4 and the product distilled in vacuo yielded 46% IV, m. 121-3° (alc.). IV (22 g.) and 10.2 g. Na in 100 ml. PhMe refluxed 2.5 hrs. with 29 g. (Me2CHCH2)2CHOH according to Beets (C.A. 45, 9502d) and the mixture treated with 5 g. carbinol, refluxed 1.5 hrs. and treated with another 5 g., the mixture worked up and the solvents evaporated, the product treated with 20.66 g. BzCl in 23 g. C5H5N and the crude benzoate fractionated from alc. gave 0.61 g. IV, 15.4 g. benzoate (IX), m. 99.5-9.9°, and 1.3 g. benzoate, m. 87.4-8.1°. Treatment of the hydrogenolysis product (X) with 3,5-(O2N)2C6H3COCl gave the dinitrobenzoate (XI), m. 108.7-9.3°

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(alc.), sapond. to yield 98.7% mixt. of stereoisomeric alcs. (XII), also obtained by sapon. of IX. Formation from VIII and the characteristic spectrum, λmax. 260, λmin. 235 mμ (log ε 2.250, 1.513), showed IV to be 8a-phenyl-1,3,6-trioxadecahydronaphthalene, as confirmed by hydrogenolysis to 3-hydroxymethyl-4-phenyltetrahydropyran XII. The cis configuration was assigned to IV and the bi-equatorial configuration to IX and XI. VII (2.46 g.) refluxed 30 min. with 3 ml. MeOH and 3 ml. 36% HCl and the washed oily layer fractionated in vacuo gave 0.6 g. solid fraction, recrystd. (alc. and petr. ether) to give VIII, showing VII, 4-hydroxyethyl-4-phenyl-m-dioxane, to be the cyclization product of the triol PhC(CH2CH2OH)2OH with HCHO. V (25 g.) treated with 10.4 g. Na, 28.8 g. (Me2CHCH2)2CHOH and 125 ml. PhMe as above and 28 g. carbinol added during the 10 hrs. reflux period, worked up and the product (21.85 g.) partially (3.57 g.) converted to the benzoate, m. 80.1-80.6° (alc.), the crude hydrogenolysis product (16.9 g.) treated with H3BO3 and the mixt. distd., the ester (10.2 g.) hydrolyzed and fractionated gave an alc., C13H18O3 (XIII), b3 175-6°, n20D 1.5360. XIII (2.06 g.) heated 1.5 hrs. at 95-100° with 50 ml. 8N H2SO4 in a stream of air gave HCHO, characterized as dimedob deriv., m. 187.0-7.5°. The reactions proved that only 1 hydrogenolyzable O atom was present and that all O atoms are combined in 2 m-dioxane rings. It was concluded that V, λmax. 260, λmin. 235,285 mμ (log ε 2.216, 1.512, 0.588), is 4-(5-m-dioxanyl)-4-phenyl-m-dioxane, converted by hydrogenolysis into 3-(5-m-dioxanyl)-3-phenylpropanol XIII. IV and V are formed by 3 successive reactions with HCHO. As no ramification is present in II the initial step in HCHO condensation can be followed only by reversal of the reaction or formation of a new double bond as in >CHCH:C(CH2OH)-. H2SO4 (180 g.), 514 g. 35% HCHO, and 360 g. (HCHO)n stirred 30 min. at 90° with addn. of 312 g. II and the mixt. stirred 30 hrs. at 90°, the cooled mixt. worked up and the product fractionated at 3 mm. from 99 g. undistillable material gave 60.3% 4-phenyl-m-dioxane and 73.5 g. fractions, b3 150-60°, n20D 1.5250-70, sepd. (66.5 g.) with H3BO3 into 29 g. nonalc. unknown compds. and 36 g. ester, hydrolyzed to an alc. (XIV); benzoate, m. 91.6-2.0°, identical with the recently described (C.A. 50, 12059d) benzoate of 5-hydroxymethyl-4-phenyl-m-dioxane, demonstrating that the formation of a new double bond in the primary reaction product with HCHO is possible, although an extremely slow reaction.

ACCESSION NUMBER: 1959:23328 CAPLUS
DOCUMENT NUMBER: 53:23328
ORIGINAL REFERENCE NO.: 53:4280i,4281a-i,4282a-c
TITLE: Reaction of α-methylstyrene with formaldehyde
AUTHOR(S): Beets, M. G. J.; van Essen, H.
SOURCE: Recueil des Travaux Chimiques des Pays-Bas et de la Belgique (1957), 76, 1009-20
CODEN: RTCPB4; ISSN: 0370-7539
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Aliphatic and cycloaliphatic aldehydes and ketones are prepared by dehydrogenating the corresponding primary or secondary alc. in the gaseous state at 350-500° in the presence of an alloy consisting of 65-75% Cu, 25-35% Zn, and a total of 0.1-1% Fe and/or Al and/or Bi. Thus, 200 g./hr. 98% BuOH is passed, by means of a measured delivery device into an evaporator heated at 200° and then enters a 1 l. brass contact chamber electrically heated to 400° containing 200 g. loosely rolled brass wire gauze (Cu 67.9, Zn 32, Fe 0.1%, and Al traces). The PrCHO formed by dehydrogenation enters a film evaporator heated to 100° and then a distillation column (provided with a cooling device) into a condensation chamber, while the H (45 l./hr.) is washed with water and enters a gasometer. The products boiling above 100° accumulated in the sump of the film evaporator (BuOH and PrCO2Bu) reenter the evaporator through a siphon, thus returning to the cycle. A yield of 189 g. (98.5%)/hr. product containing 98% PrCHO, and 0.2% MeCH:CHCHO is obtained. With this apparatus can be produced RCHO, where R = Et, Pr, iso-Pr, iso-Bu, n-C5H11, n-C6H13, and n-C7H15 from the corresponding RCH2OH; Me2CO from iso-PrOH; and cyclohexanone from cyclohexanol.

ACCESSION NUMBER: 1956:82186 CAPLUS
DOCUMENT NUMBER: 50:82186
ORIGINAL REFERENCE NO.: 50:15576i,15577a-c
TITLE: Aliphatic and cycloaliphatic aldehydes and ketones
PATENT ASSIGNEE(S): Farberke Hoechst AG vorm. Meister Lucius & Bruning
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 739263		19551026	GB	

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AB MePhC:CH2 (I) and β-pinene (II) condense with CH2O and secondary amines in AcOH-H2SO4 according to the equation: -CHC:C + CH2O + HNR2 → -C:CCCH2NR2. Anethole (III) under similar conditions reacted principally with the formation of a product of the type -CHC(CH2NR2)COAc. H2SO4 (10 cc.) in 300 cc. glacial AcOH treated with cooling with 140 g. 40% aqueous Me2NH, 34.5 g. paraformaldehyde, and 118 g. I, the mixture refluxed 3 hrs. under N, cooled, neutralized with 230 g. NaOH in 600 cc. H2O, and extracted with 200 cc. Et2O, the aqueous layer washed with two 100-cc. portions Et2O, and the combined Et2O solns. washed with H2O, dried, and fractionated yielded 77 g. Me2NCH2CH2CPh:CH2, b12 110-14°, nD25 1.5226-1.5228 (oxidized with KMnO4 it gave BzOH); methiodide, m. 162-3° (from absolute EtOH); HCl salt, noncrystallizable oil. Similarly were prepared the following CH2:CPhCH2CH2R' (R', % yield, b.p./mm., and nD25 and m.p. of HCl salt given): Et2N, 8.9, 82-5°/0.3, 1.5131-1.5149, 120-2°; piperidino (IV), 28.5, 115-16°/0.20-0.25, 1.5375-1.5385, 205-6° (methiodide, m. 131-3°); pyrrolidino, 6.0, 96-7°/0.4, 1.5401, 117-19°; morpholino, 32.4, 98-101°/0.2-0.3°, 1.5421-1.5422, 177-9° (methiodide, m. 123-5°). I (35 g.) in 80 cc. 95% EtOH hydrogenated 2 hrs. at 60 lb. pressure over 5 g. Raney Ni and the mixture filtered and distilled gave 28.0 g. MePh(CH2)3NMe2, b19 112-13°, nD25 1.4940; HCl salt, m. 165-7°. Similarly were prepared the following compds. MePh(CH2)3R' (R', b.p./mm., nD25, and m.p. of the HCl salt given): Et2N, 68-70°/0.3, 1.4910-1.4915, 115-16°; piperidino, 109-12°/0.3, 1.5130-1.5135, 168-70°; pyrrolidino, 75-6°/0.3, 1.5132, 137-9°; morpholino, 95-6°/0.25, 1.5153, 177-9°. I (52.5 g.) added slowly to 117 g. concentrated H2SO4 at 5°, and the product washed and distilled gave 25 g. distillate, b2 190-2°, nD25 1.5478-1.5480, apparently 1,3-bis(dimethylaminomethyl)-1-methyl-3-phenylhydrindan. Cyclohexene, styrene, and Ph2C:CH2 subjected to the condensation with paraformaldehyde and piperidine in the presence of AcOH gave only 65, 80, and 90% yields, resp., of the unchanged starting materials. II condensed with CH2O and a secondary amine gave the corresponding nopylamines [nopyl-2-(6,6-dimethylbicyclo[1.1.3]hept-2-en-2-yl)ethyl] (% yield, b.p./mm., and nD25, and m.p. of HCl salt given): N-nopylpiperidine (V), 47.5, 101-2°/0.4, 1.4967-1.4970, 253-5°, αD20 -22.3 to -24.8° (methiodide, m. 201-2°; V.Me2SO4, 145-8°). N-Nopylpyrrolidine, 20, 82-3°/0.3, 1.4946-1.4949, 229-31°; N-nopylmorpholine, 30, 104-6°/0.3, 1.4991-1.5020, 218-20°. V in EtOH hydrogenated at 100° and 1000 lb. pressure over Pd-C yielded 55% N-dihydronopylpiperidine, b0.35 95-6°, 1.4929-1.4934, 277-82°; methiodide, m. 221-3°; methosulfate, m. 171-3°. Similarly was obtained N-dihydronopylpyrrolidine, 71%, 89-93°/0.3, 1.4911, 235-7°. Nopol (16.6 g.) in 80 cc. pyridine treated at 5° with 20.7 g. p-MeC6H4SO2Cl, the mixture held at 5° overnight, and treated with H2O, ice, and Et2O, the Et2O layer washed with dilute HCl, and H2O, dried and evaporated, the crude residue refluxed 2 hrs. with 25 g. piperidine in 80 cc. Me2CO, allowed to stand overnight, and diluted with 200 cc. Et2O, and the precipitate (20.5 g.) recrystd. from EtOAc-EtOH gave piperidine p-toluenesulfonate, m. 130-2°; the Et2O-Me2CO filtrate treated slowly with 50 cc. concentrated HCl, and the precipitate (22.5 g.) recrystd. twice from H2O yielded V.HCl, m. 252-5°

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(decompn.); free V, b0.3 93-5°, nD25 1.4952-1.4960, αD20 -18.80° (1 dm., neat). III (148 g.), 37.5 g. paraformaldehyde, and 10 cc. concd. H_2SO_4 in 400 cc. glacial AcOH refluxed 9.5 hrs., 150 cc. AcOH distd. off at 15 mm., the residual mixt. dild. with 500 cc. Et_2O, the soln. treated dropwise with cooling with 185 g. NaOH in 600 cc. H_2O with stirring, the aq. layer extd. with 300 cc. Et_2O, and the combined Et_2O layer and ext. washed, dried, and fractionated yielded 30 g. 1-(p-methoxyphenyl)-2-methyl-3-piperidino-1-propyl acetate (VI), b0.4 146-7°, nD25 1.5140, and m. 53-4° (from aq. EtOH). The solid and the liquid VI gave the same HCl salt, m. 173-4° (decompn.). Another run with III gave VI, b0.5 160°, nD25 1.5169-1.5172. VI oxidized with alk. $KMnO_4$ gave p-$MeOC_6H_4CO_2H$, m. 182-4°. VI refluxed with KOH in aq. EtOH, the mixt. dild. with H_2O, the ppt. oil taken into Et_2O, the soln. washed, dried, and treated with dry HCl, and the gummy ppt. washed with EtOAc and recrystd. from Me_2CO gave 1-(p-methoxyphenyl)-2-methyl-3-piperidino-1-propanol (VII) HCl salt, m. 170-2°. VI.HCl allowed to stand several weeks in Me_2CO-EtOAc gave prisms, m. 120-1°, and needles, m. 172-4°; the 2 diastereoisomeric alc. HCl salts crystd. apparently separately. VII (3.32 g.) and 1.24 g. $Na_2Cr_2O_7$ in 35 cc. AcOH heated slowly to 80°, chilled, covered with Et_2O, and treated with 50 g. NaOH in 100 cc. H_2O, the Et_2O layer washed, dried, and treated with dry HCl in Et_2O, and the pptd. semisolid gum crystd. from Me_2CO-abs. EtOH gave 1-(p-methoxyphenyl)-2-methyl-3-piperidino-1-propanone-HCl, m. 173-5° (decompn.) (sealed tube).

ACCESSION NUMBER: 1956:27968 CAPLUS
DOCUMENT NUMBER: 50:27968
ORIGINAL REFERENCE NO.: 50:5676g-i,5677a-h
TITLE: The reaction of formaldehyde and secondary amines with some olefins
AUTHOR(S): Hennion, G. F.; Price, Charles C.; Wolff, Vernon C., Jr.
CORPORATE SOURCE: Univ. of Notre Dame, Notre Dame, IN, USA
SOURCE: Journal of the American Chemical Society (1955), 77, 4633-6
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English

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AB Cresols and chlorophenols were condensed with Me_2NH (I), Et_2NH (II), morpholine (III), or piperidine (IV). In all the products substitution took place in the o-position to the phenolic OH, although the moderate yields allow for the possibility that other products, not isolated, were also formed by a different substitution mechanism. All the products from I or III were soluble at room temperature in 5% NaOH while those from II or IV were generally insol. The strong amine bases were sufficiently active to mask the phenolic behavior. The products were tested and found inactive as antimalarials. In preparation method (A), equimolar amts. of the phenol, 40% CH_2O, and I or II were allowed to stand in alc. for several hrs., refluxed 2 h., concentrated, taken up in Et_2O, extracted with 2N HCl, made basic, extracted with Et_2O, and the extract washed, dried, and fractionated after evaporation of the solvent. In method (B), the phenol, CH_2O, and III or IV in alc. were refluxed 1-2 h. with a small amount of concentrated HCl and worked up as in (A).

The following X-substituted (2-hydroxybenzyl)dimethylamines were prepared (X, m.p., b.p./mm., % yield, and m.p. of the picrate and HCl salt given): 3-Me, -, 78-85°/0.3, 50, -, 129°; 4-Me, 44°, 99°/0.2, 60, -, hygroscopic; 5-Me, -, 88°/1, 68, 168°, 156°; 3-Cl (V), -, 117°/1.7, 30, 167°, 167°; 4-Cl (VI), -, 103°/0.5, 40, 159, hygroscopic; 5-Cl, -, 92°/0.1, 68, -, 165° [from anhydrous Et_2O-EtOH (VII)]; 3,5-Cl_2, 60° (from EtOH), -, 30, -, 185°. Prepared similarly were the following X-substituted (here and subsequently in this abstract the X substituent is in the benzyl group) (2-hydroxybenzyl)diethylamines : 3-Me, -, 93-7°/0.5, 30, -, 153°; 4-Me, -, 107°/0.5, 36, 142°, 108°; 5-Me, -, 100-5°/0.1, 40, -, 152°; 3-Cl, -, 105-10°/2, -, -, 151° [from absolute C_6H_6-EtOH (VIII)]; 4-Cl, -, 120°/2, -, 162°, 123°; 5-Cl, -, 122°/1, 56, -, 150°; 3,5-Cl_2, -, 130-40°/0.5, -, -, 170° (from VIII); the following X-substituted 1-(2-hydroxybenzyl)piperidines: 3-Me, -, 110°/0.2, -, 184°, 186°; 4-Me, 55° [from aqueous EtOH (IX)], -, 21.5, 132°, 183°; 5-Me, -, 115°/0.2, -, 150°, 188°; 3-Cl, 49° (from IX), -, 15, -, 185°; 4-Cl, -, 156°/5, 15, -, 204° (from VII); 5-Cl, 57° (from IX), -, 18, -, 232°; 3,5-Cl_2, 80° [from petr. ether (X)], -, 70, -, 192°; the following X-substituted 4-(2-hydroxybenzyl)morpholines: 3-Me, -, 120°/0.5, 15, 201°, 196° (from VII); 4-Me, 64° (from IX), -, 21, 165°, 190° (from VII); 5-Me, 54° (from X), -, 25, -, 204°; 3-Cl, 114° (from EtOH), -, 44.5, 201°, 197°; 4-Cl, 57° (from X), -, -, -, 178°; 5-Cl, 60° (from X), -, 20,202°, 191°; 3,5-Cl_2, 89° (from IX), -, -, -, 200°. Also prepared by this method were 90% 1-(2-hydroxy-1-naphthylmethyl)-piperidine, m. 95° (HCl salt, m. 145°), and 89% 4-(2-hydroxy-1-naphthylmethyl)morpholine (XI), m. 115° (from IX), (HCl salt, m. 177°). In the structure proofs, 8 g. V and 4 g. Cu chromite in 100 cc. dioxane were heated 5 h. at 150° in an autoclave under 130 kg. H, cooled, the catalyst was filtered off, most of the solvent evaporated, the residue poured into H_2O, extracted with Et_2O, and the extract dried, freed of solvent, and distilled, giving 2 g. of a mixture of o-cresol and 6,2-ClMeC6H3OH. The phenols, e.g. 5,2-ClMeC6H3OH, were converted to the corresponding phenoxyacetic acids, e.g. 5,2-$ClMeC_6H_3OCH_2CO_2H$, of which 0.4 g. with 1.2

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g. Raney Ni in 2 cc. alc. treated in portions with 12 cc. 2N NaOH, boiled, cooled, filtered, and acidified with dil. H_2SO_4, gave 0.25 g. o-$MeC_6H_4OCH_2CO_2H$ (XII), m. 149° (mixed m.p. with authentic sample, 150°). VI treated similarly also gave XII, thus establishing the o-directed substitution in the Mannich bases. XI (4.8 g.) and 3.6 g. CH_2ClCO_2Et added to 0.46 g. Na in 20 cc. abs. EtOH, refluxed 1 h., the alc. evapd., and the residue treated with H_2O, extd. with Et_2O, dried, concd., and treated with dry HCl gave 35% Et (1-morpholinomethyl-2-naphthyloxy)acetate H Cl salt (XIII), m. 185° (from VII). XIII and several of the Mannich bases (no details given) were found inactive toward plants in the "pea test" and in a test on elongation of corn roots.

ACCESSION NUMBER: 1956:27718 CAPLUS
DOCUMENT NUMBER: 50:27718
ORIGINAL REFERENCE NO.: 50:5547c-i,5548a-b
TITLE: A study of the Mannich reaction between some substituted phenols and secondary amines
AUTHOR(S): Julia, Marc; Tchernoff, Georgette
CORPORATE SOURCE: Ecole polytech., Paris
SOURCE: Bulletin de la Societe Chimique de France (1955) 830-3
CODEN: BSCFAS; ISSN: 0037-8968
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 50:27718

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AB cf. C.A. 50, 779h. An investigation to ascertain the influence of structural and elec. factors upon the mode of cleavage of substituted allyl ethers by Grignard reagents indicated that aryl and alkyl (lower than C_7H_{15}) Grignard reagents cleave substituted allyl ethers by a 1,2-mechanism, while $C_7H_{15}MgBr$ and $C_8H_{17}MgBr$ cleave both mono- and disubstituted allyl ethers by a 1,4-mechanism. The condensation of the appropriate Na alkoxide and alkyl halide gave the following allyl ethers (b.p./mm., nD20, d20, and M RD) given): $PhCH_2CH_2OCH_2CH{:}CH_2$ (I), 115-16°/37, 1.5200, 1.0015, 49.14; $PhCH_2CH_2OCH_2CH{:}CHPh$ (II), 121-3°/3# (70-4°/1), 1.5390, 1.0019, 74.40; $BuOCH_2CH{:}CHPh$ (III), 132-4°/13, 1.5510, 0.9841, 61.73. The appropriate aldehydes and grignard reagents condensed and the resulting secondary alc. converted to the Na derivs. and treated with the suitable alkyl halide gave the following allyl ethers (same data given): $BuOCHBuCH{:}CH_2$ Me (IV), 179-81°/748, 1.4328, - (d22 0.8210), 58.27; $Me_3COCH(CMe_3)CH{:}CHMe$ (V), 164-5°/752 (104°/60), 1.4671, 0.8960, -. The appropriate allyl ether (3-5 g.) in 50-75 cc. hexane treated with ozone at 0° the mixture decomposed with Zn dust, H_2O, traces of hydroquinone, and $AgNO_3$, and the products isolated as described previously (C.A. 49,833c) gave the corresponding aldehydic cleavage products (the 2 aldehydes formed, their b.p./mm., nD20, d20, and the m.p. of their 2,4-dinitrophenylhydrazones given): II, BzH, 55-6°/50, 1.4600, 0.999, 236-7° and $PhCH_2CH_2OCH_2CHO$, 94-5°/10, 1.5105, 1.282,111-12°; III, BzH, 145-7°/700, 0.986, 1.4700, 238-9°, and $BuOCH_2CHO$, 130-2°/746, 1.4289, 0.854, 89-90°; IV, AcH, -, -, -, 147-9°, and Bu(BuO)CHCHO, 90-3°/29 (153-4°/756), 1.4230, 0.915, 96-7°; V, AcH, -, -, -, 145-6° and $Me_3CCH(CMe_3)CHO$, 132-3°/753, 1.4279, 0.884, 87-8°; $BuOCH(CH_2Ph)CH{:}CHPh$ (VI), BzH, 164-5°/749, -, 0.925, 235-6°, and $PhCH_2CH(OBu)CHO$, 110-12°/749, 1.4180, 0.848, 99-100°. The appropriate allyl ether in Et_2O or C_6H_6 added to the suitable Grignard reagent during 2-4 h. the mixture refluxed 20-40 h., and hydrolyzed with saturated aqueous NH_4Cl, the aqueous layer extracted continuously with Et_2O, the organic layer and the extract combined, dried, and evaporated, and the residue distilled gave the corresponding olefin and alc. I and $C_6H_{13}MgBr$ gave 22% 1-nonene (VII), b748 143-6°, nD20 1.4261, d20 0.8155, and 94% $PhCH_2CH_2OH$ (VIII), b748 201-3°, nD20 1.5179, d20 1.0001, M RD 37.08 (3,5-dinitrobenzoate, m. 105-6°). II and $C_6H_{13}MgBr$ gave 15% 1-phenyl-1-nonene (IX), b746 140-3°, nD20 1.4261, d20 0.8323, and 23% VIII. II and PhMgBr yielded 17% $PhCH_2CH{:}CHPh$ (X), b15 112-15°, nD20 1.5501, d20 1.0019, M RD 62.48, and 98% VIII. II and $PhCH_2MgBr$ gave 47% $PhCH_2CH_2CH{:}CHPh$ (XI), b13 145-8°, nD20 1.5639, d20 1.0172, M RD 66.58, and 83% VIII. III and $PhCH_2MgBr$ yielded 41% XI, b6 98-9°, and 25% BuOH, b745 112-15° (3,5-dinitrobenzoate, m. 68-9°). III and $C_8H_{17}MgBr$ gave 24% 3-phenyl-1-undecene (XII), b753 145-6°, nD20 1.5050, d20 0.876, M RD) 77.79, and 88% BuOH. IV and EtMgBr yielded 83% $MeCH{:}CHCHBuEt$ (XIII), b742 188-9°, nD20 1.4339, d20 0.805, M RD 45.28, and 23% BuOH. IV and BuMgBr gave 68% $MeCH{:}CHCHEtPh$ (XIV), b748 180-2°, nD20 1.4440, d20 0.8408, and 35% BuOH. V and $C_8H_{17}MgBr$ yielded $Me_3CCH{:}CHCHMeC_8H_{17}$ (XV), b753 135-8°, nD20 1.4305, d20 0.7822, M RD 74.03, and 88% Me_3COH, b753 83-5° (3,5-dinitrobenzoate, m. 140-1°). V and PhMgBr gave 30% $MeCH{:}CHCHPhCMe_3$ (XVI), b752 171-3°, nD20 1.5040, d23 0.9880, and 30% Me_3COH. VI and $C_8H_{17}MgBr$ yielded 59% $PhCH_2CH{:}CHCHPhC_8H_{17}$ (XVII), m. 49.5-50°, and 63% BuOH. The olefinic reaction products were identified by ozonization. The olefins used in the ozonization and the 2 aldehydes formed were (b.p./mm. and nD20 of the

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aldehydes and the m.ps. of their 2,4-dinitrophenylhydrazones given): VII, CH2O, -, -, 165-6° , and C7H15CHO (XVIII), 100-1° /700, 1.4278, 106-7°; IX, BzH, 100-2°/700, -, 233°, and XVIII; X, BzH and PhCH2CHO, -, -, 120-1°; XI, BzH and Ph(CH2)2CHO, -, -, 144-5°; XII, CH2O and 2-phenylcapraldehyde, 101-2°/733, 1.4111, 122-3° (see below); XIII, AcH, -, -, 145-6°, 2-ethylcaproaldehyde, -, -, 119-20°; XIV, AcH, and 2-phenylcaproaldehyde, 120-1°/742, 1.3979, 107-8° (d20 0.879); XV, Me3CCHO, 81-2°/744, 1.3709, (d23 0.817), 103-4°, and 2-methyldecanal, 119-20°/744, 1.4205 (d23 0.8948), 63-4°; XVI, AcH and 2-phenyl-3,3-dimethylbutanal, 115-18°/744, -, 70-1°; XVII, PhCH2CHO, 179-81°/748, -, 121-2° and 2-phenylcapraldehyde, -, -, 85-6° (sic).

ACCESSION NUMBER: 1956:23948 CAPLUS
DOCUMENT NUMBER: 50:23948
ORIGINAL REFERENCE NO.: 50:4835a-i,4836a-b
TITLE: Grignard reagents and unsaturated ethers. V. Mode of cleavage of α- and γ-substituted allyl ethers by Grignard reagents
AUTHOR(S): Hill, Carl M.; Simmons, Doris E.; Hill, Mary E.
CORPORATE SOURCE: Tennessee A. & I. State Univ., Nashville
SOURCE: Journal of the American Chemical Society (1955), 77, 3889-92
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB A primary or **secondary** alicyclic amine with HCHO and HCO2H produces an alicyclic tertiary amine, RNMeR' where R is a cycloalkyl group and R' is an alkyl or cycloalkyl group. To 119.5 parts 85% HCO2H at 5° was added 99.2 parts cyclohexylamine, then 179 parts 37% HCHO, with the temperature kept at 5-10°, and the mixture stirred and heated to 56° until CO2 was evolved, whereupon heating was discontinued; the temperature rose about 26°. When the exothermic reaction was over, the mixture was heated 3.5-4 hrs. at 90-5°, cooled to 50°, 126 parts concentrated HCl added, and the excess HCHO and HCO2H removed by distillation, the vapor temperature reaching 108°. To the residue was added 242 parts 25% NaOH, and the resulting upper layer distilled to give 2 fractions (I and II). I, b. 95-6°, contained 2 layers; the organic layer was dried and added to II which b. 158-9° and was N,N-dimethylcyclohexylamine (yield, 80-3%).

ACCESSION NUMBER: 1955:73637 CAPLUS
DOCUMENT NUMBER: 49:73637
ORIGINAL REFERENCE NO.: 49:14027d-f
TITLE: Tertiary alicyclic amines
PATENT ASSIGNEE(S): Monsanto Chemical Co.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 716649		19541013	GB	

L19 ANSWER 46 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB The condensation of CH2O and **secondary** amines with thiophenols yielded aryl dialkylaminomethyl sulfides (I) and not the expected Mannich bases. The picrates of the I are described, p-O2NC6H4COCl formed stable compds., presumed to be sulfonium salts, with the I obtained from p-MeC6H4SH and the thionaphthols, whereas from the other I only the p-nitrobenzoate of the original thiophenol could be isolated. 2,5-Br2C6H4SO2Cl reduced with Zn yielded 50% 2,5-Br2C6H3SH, m. 39-40°. The appropriate **secondary** amine added dropwise to an equimolar amount of the thiophenol below 20° (in most cases a precipitate of the addition product appeared), the mixture treated with an equivalent amount 37% aqueous CH2O, heated during 1 h. up to 80°, kept 2 h. at 80°, and cooled, and the solid deposit recrystd. from EtOH or ligroine gave the desired I; if the crude product was an oil, the oil was extracted into Et2O, the solution dried with MgSO4 and evaporated at 20 mm. pressure and about 50°, and the residue **distilled** in vacuo. In this manner were prepared the following aryl piperidinomethyl sulfides (aryl group, m.p. or b.p./mm., % yield, and m.p. of picrate given): Ph, 138-41°/5-6, (n25D 1.5789, d30 1.0520), 67, 142-3°; o-MeC6H4, 133-5°/2-3, 45, 149-51°; m-MeC6H4, 141-2°/2-3, 64, 133-4°; 2-C10H7 (II), 48-9°, 89, -; 1-C10H7, (III), 136-7°, 89, -; p-O2NC6H4, 90-3° (from ligroine), 59, -; p-ClC6H4, 47-9°, 43, 160-1°; p-BrC6H4, 54-5°, 44, 162-3°; 2,5-Br2C6H3, 39-40°, 47, 157-8°; p-MeOC6H4, 127-31°/4-5, 38, 145-6°; p-MeC6H4 (IV), 32-2.5°, -76, -; 2,4,6-Me3C6H2, 46-7°, 22, 179-81°; the following aryl morpholinomethyl sulfides (same data given): Ph, 146-9°/5-6, (n25D 1.5809, d30 1.1251), 33, 132-3°; o-MeC6H4, 138-40°/2-3, 54, 159-60°; m-MeC6H4, 133-7°/2-3, 79, 145-7°; 2-C10H7 (V), 47-8°, 96, -; 1-C10H7 (VI), 73-4°, 88, -; p-O2NC6H4, 79-81° (from ligroine), 70, -; p-ClC6H4, 60-1° 79, 172-3°; p-BrC6H4, 66-6.5°, 69, 172-4°; 2,5-Br2C6H3, 84-5°, 61, 174-5°; p-MeOC6H4, 50-1°, 73, 158-9°; p-MeC6H4 (VII), 38-8.5°, 96, -; 2,4,6-Me3C6H2, 60-2°, 26, 174-5°; and the following aryl diethylaminomethyl sulfides (same data given): Ph, 110-12°/5-6, (n25D 1.5500, d30 0.9878), 71, 87.5-89°; o-MeC6H4, 115-17°/2-3, 67, 108-10°; m-MeC6H4, 114-17°/2-3, 55, 87-9°; p-ClC6H4, 135-8°/2-3, 43, 124-5°; p-BrC6H4, 110-15°/2-3, 38, 127-8°; 2,5-Br2C6H3, 122-4°/4-5, 31, 112-13°; p-MeOC6H4, 107-10°/4-5, 40, 110-11°; p-MeC6H4, 113-14°/2-3, (n20D 1.5481, d30 0.9804), 58, -; 2,4,6-Me3C62, 138-40°/3-4, 40, 149-50°; all compds. were recrystd. from EtOH except where stated otherwise. The appropriate I (15 g.) in 100 cc. dry PhMe was treated with 11 g. p-O2NC6H4COCl in 50 cc. dry PhMe, the mixture refluxed 2 h., and the resulting addition product, presumed to be a sulfonium salt, recrystd. from 95% EtOH. In this manner were prepared the p-O2NC6H4COCl-I addition products (m.p. given) from the following I: IV, (adduct = C20H23ClN2O3S), 108-9°; VII, 155-5.5°; VIII, 193-4°; II, 159-60°, V, 176-8° (all from EtOH); III, 198-200° (from 1:1 dioxane-EtOH by adding H2O); VI, 180-2° (from 6:4 dioxane-EtOH). The following I (aryl group given) gave under the same conditions only the p-nitrobenzoates of the corresponding thiophenols (m.p. and % yield given): p-ClC6H4, 144-5°, 57; p-BrC6H4, 179-9.5°, 54; 2,5-Br2C6H4, 146-7°, 49; p-O2NC6H4, 150-3°, -; p-MeOC6H4, 120-1°, 63; 2,4,6-Me3C6H2 (IX), 94-6°, 55; all esters were recrystd. from 95% EtOH. The

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p-nitrobenzoates did not sep. from the cooled PhMe solns.; the solns. were, therefore, concd. to beginning crystn. The esters were also synthesized independently from the chloride and the thiophenols in 50-60% yields. IX was prepd. by dissolving the thiophenol in 10% aq. NaOH, adding a slight excess of p-O2NC6H4COCl, shaking the mixt. 2 h., and recrystg. the yellow solid product from 95% EtOH.

ACCESSION NUMBER: 1955:53525 CAPLUS
DOCUMENT NUMBER: 49:53525
ORIGINAL REFERENCE NO.: 49:10279g-i,10280a-f
TITLE: The condensation of thiophenols with **secondary** amines and **formaldehyde**
AUTHOR(S): Grillot, Gerald F.; Felton, Herman R.; Garrett, Beverley R.; Greenberg, Harold; Green, Richard; Clementi, Robert; Moskowitz, Mark
CORPORATE SOURCE: Syracuse Univ., Syracuse, NY
SOURCE: Journal of the American Chemical Society (1954), 76, 3969-71
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 49:53525

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AB cf. C.A. 46, 3844c. Different methods for preparing pure solns. of HCHO (I) are discussed, and the best conditions necessary for obtaining solns. of a high degree of purity are described. The conditions under which polyoxymethylene (II) of various degrees of polymerization (d.p.) can be prepared are then described. Finally the reactions which take place when polyoxymethylenes are dissolved in water in the absence and in the presence of acids and bases are indicated, and the existence of maximum points on the concentration-time curves of products of low d.p. is explained. In purifying I by distillation of com. I containing MeOH, not all MeOH can be eliminated under any conditions, and, contrary to Natta and Baccaredda (C.A. 27, 4996), e.g., aqueous I containing 5-6% MeOH, distilled to 0.25 volume, gives a residue containing 0.5% MeOH. This is the min. obtainable because of continuous formation of MeOH and HCO2H (III), irrespective of the pH. If the solution is buffered by CaCO3 or MgCO3, much more MeOH is formed. When 0.5% MeOH is unobjectionable, the method is rapid and efficient with a tall fractionating column. The distillation residue is neutralized, 0.4% NaOH added, the mixture allowed to stand 2 days, filtered, and the precipitate washed with water, and dried over P2O5, yielding an amount of pure II corresponding to approx. 0.5% of the I. II is difficult to dissolve in water, e.g., to prepare as 25% solution it must be refluxed 4 days, and then the solution contains 0.4% III. But II in 0.1N H2SO4 refluxed 3-4 hrs., or a suspension of II in 0.1N NaOH agitated 10 min., brought to pH 2-3 with H2SO4, and filtered, gives a 15% solution of I, which, when distilled, yields solns. of I having pH 3-3.5 and containing only 0.05% III. In the preparation of II from concentrated aqueous I (cf. C.A. 46, 8494h), various d.p. values can be obtained at room temperature thus: 15-fold from 40% I at pH 7 in 4-6 hrs.; 30-35-fold under the same conditions in 50-70 hrs., and 80 to 100-fold from 35% I at pH 9-10 in 30-40 days. The solubilization of II was studied, not under the restricted conditions of Lobering (C.A. 30, 7978.1) or Sauterey (C.A. 46, 7854i), but at 20° with wide ranges of concentration in 0.1N NaOH and of time, and with highly purified II of various d.p. values. When the concentration of I is plotted against time, maximum concns. of I are evident for all polymers (the higher the d.p. the lower this maximum), and all concns. decrease asymptotically to the same ultimate concentration (18%) with time. Evidence shows that this decrease is not attributable to the formation of II and III nor to other reactions, such as aldol condensation. I solns. are of 3 types. (1) Unstable solns., i.e., of concns. above the stability limit (s.l.), from which II of 7-10 d.p. seps. (2). Below this concentration, metastable solns. with supersatn. only of II of higher mol. weight, exist and these represent the true equilibrium concentration (e.c.) of the heterogeneous solid II-aqueous I system. (3) Stable solns., of concns. below the e.c., not saturated with II. Preliminary expts. indicate that the dissociation tension (d.t.) of the equilibrium, HO(CH2O)nH .dblarw. HO(CH2)n-1H + I, decreases with increase of the mol. weight of II. II with low d.p. in contact with metastable solns. undergo an "aging" process, with resulting increase of mol. weight, because their d.t. is less than the partial pressure

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of the I in soln. These facts make possible an easy interpretation of the phenomena when solid II is in contact with water (neutral, acidic, or alk.). The higher the temp., the higher the e.c. and s.l. The expts. were performed at 20°, and at this temp. the e.c. is approx. 18% and the s.l. concn. 35%. The mean d.p. of the II as ppt. is around 50, and that of II sepd. from more concd. solns. is 7.5-9. The d.p. of the 35% soln. (satd. with II) is 7-9. During the period when the concn. of a soln. of II of d.p. 8 is increasing, primary and secondary phenomena occur. Unaltered II reaches 0.67% concn., then detaches terminal I groups until the partial tension of the I equals the d.t. of II. The following hydrolysis may occur: HO(CH2O)8H + H2O → HO(CH2O)7H + H2C(OH)2 (IV); this is catalyzed by H and OH ions. Anhyd. and hydrated I and II are subsequently transformed, because the soln. must reach an equil. between the various II products, IV, and anhyd. I. These secondary reactions also are catalyzed by H and OH ions, and the rate at which concd. solns. are obtained depends on their concn. (cf. Lobering, C.A. 30, 7978.1). Solubilization proceeds by these mechanisms until the partial tension of HCHO reaches the d.t. of the sepd. II. If the initial ratio of water to II is such that this tension is not attainable, all II dissolves. But if this tension is reached with II still not in soln., other reactions take place which reduce the concn. With respect to soln. of II having d.p. 50, the same phenomena are observed, except that when the soln. is satd. with II and the partial tension of I equals the dissocn. tension of the ppt., the latter does not "age", because at equil. the soln. is not satd. with higher polymers. The total concn. at equil. is a function of the concn. of anhyd. I, i.e., of the tension of the insol. component. Hence, the concn.-time curve has no max. In practice, certain divergences from these phenomena are to be expected for reasons which are discussed.

ACCESSION NUMBER: 1954:52799 CAPLUS
DOCUMENT NUMBER: 48:52799
ORIGINAL REFERENCE NO.: 48:9318d-i,9319a-e
TITLE: The system: water-formaldehyde. V. Preparation of pure solutions of formaldehyde, and the separation and redissolution of polyoxymethylenes
AUTHOR(S): Iliceto, Antonio
CORPORATE SOURCE: Univ. Padova, Italy
SOURCE: Gazzetta Chimica Italiana (1953), 83, 18-27
CODEN: GCITA9; ISSN: 0016-5603
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB Three principal factors control β-hydroxy carbonylation (aldol and ketol condensation): (1) enolization with a basic or acidic catalyst; (2) induced cationoid character of alternate C atoms in a chain; and (3) steric effects. The cationoid effect is especially pronounced in aldehydes. Mixed aldehyde-ketone condensations are facilitated by the fact that the α-C of the ketone is a strong electron donor and the carbonyl C of the aldehyde is a strong electron acceptor. The principal reaction product of RCHO with R'CH2COCH2R'' is RCH(OH)CHR'COCH2R''. Three types of mixed ketolization are distinguished: (1) vinyl ketone and aldehyde with high concentration of soda (10% aqueous), (2) Powell type, with cautious introduction of aldehyde, low catalyst concentration, in alc., and (3) Grignard-Dubien type, aqueous and ethereal, with high catalyst concentration and cautious and progressive introduction of aldehyde. Powell type ketolizations were performed by maintaining the ketone at constant temperature in a Mariotte flask with shaking, adding the catalyst as alc. KOH, introducing AcH slowly as vapor, neutralizing with (CO2H)2, and distilling The yield of AcCH2CH(OH)Me (I) from AcH and Me2CO decreased from 55% at 15° to 0% at 70° (5:1 Me2CO-AcH molar ratio and about 0.7% KOH), increased from 35.7% to 84% with an increase in Me2CO-AcH molar ratio to 2.25:13.2 (at 12.5-15° with 1% KOH) and decreased linearly from 84 to 46% with an increase in KOH concentration from 0.37 to 2.8% (5:1 Me2CO-AcH). Condensation of CH2O with ketones was difficult because of resinification but fair yields of ketols were obtained with the aid of anhydrous CH2O. AcEt (144 g.), 30 g. 30% CH2O in EtOH, and 3 g. K2CO3 agitated 12 hrs. at 22° gave 38 g. AcCHMeCH2OH (II). AcPr and CH2O similarly gave 45% AcCHEtCH2OH (III), n14 1.4377, d11.511.5 0.979, b16 96-103°. II (20 g.) and 4 g. ZnCl2 on distillation gave 10 g. AcMe:CH2, b. 76°. III similarly gave AcCEt:CH2 (IV), b. 114-17°. Hydrogenation of IV in the presence of Raney Ni-Pt gave AcCHEtMe, b732 114-17°; semicarbazone, m. 94-5°. AcCHMe2 and CH2O as in preparation of II gave 40% AcCMe2CH2OH, b15 85°. AcCMe3 and CH2O did not give an identifiable ketol. AcAm and CH2O gave 42% AcCHBuCH2OH (V), b12 112-14°, d1414 0.927, n15 1.438. V and ZnCl2 gave the corresponding vinyl ketone which on hydrogenation gave AcCHMeBu, b. 162°; semicarbazone, m. 80°. AcC6H13 and CH2O gave 46% AcCHAmCH2OH, b14 128°, d1313 0.933, n20 1.442. iso-PrCHO (144 g.), 580 g. Me2CO, and 70 ml. N Na2CO3 stirred 7 hrs., neutralized with (CO2H)2, and vacuum distilled gave 38 g. iso-PrCH(OH)CH2Ac, b13 85-7°. Chemical properties of two secondary β-ketols, I and MeCOCHMeCH(OH)Me (VI), were studied in detail. Thermal stability of the pure ketols is good: I can be distilled at atmospheric pressure and VI yellows only slightly after 36 hrs. at 95°. In even feebly alkaline medium they slowly decompose into the original ketone and aldehyde. Distn from acidic medium and treatment with AcCl cause dehydration to vinyl ketones. VI (50), 50 g. Ac2O, and 1 drop C5H5N distilled, the distillate (b13 88-91°) washed with H2O, dried, and redistd. gave 35 g. VI acetate, b12 88-92°, d2615 0.980. Reaction with dinitrophenylhydrazine gave the following hydrazones (ketone and m.p. given): AcCH:CHMe, 155°; AcCMe:CHMe, 194°; AcCEt:CHMe, 161°. p-IC6H4CONHNH2 gave the following derivs. (ketone and m.p. given): I, 133-4°; VI, 150°; II, 84-5°. The p-carboxyphenylhydrazone of II formed similarly.

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Ketols (0.2 mole in 150 ml. EtOH) were hydrogenated in the presence of 10 g. Pt-activated Raney Ni and 0.1 ml. 10N Na2CO3 soln. at atm. pressure to give from: II, 92% MeCH(OH)CHMeCH2OH, b14 102-3°; I, 70% MeCH(OH)CH2CH(OH)Me, b17 103°; EtCH(OH)CH2Ac, 78% EtCH(OH)CH2CH(OH)Me; isoBuCH(OH)CH2Ac, 90% iso-BuCH(OH)CH2CH(OH)Me, b16 113°, d2113 0.936, n21 1.441; VI, 80% MeCH2(OH)CHMeCH(OH)Me, b10 103-5°; AcCHEtCH(OH)Me, MeCH2(OH)CHEtCH(OH)Me, b. 208°; AcCMe2CH(OH)Me, incomplete reaction because of steric hindrance; Me2C(OH)CH2Ac, 82% Me2C(OH)CH2CH(OH)Me, b12 102°; EtCOCH2C(OH)MeEt, 91% EtCH(OH)CH2C(OH)MeEt, b12 112-14°, d2113 0.929, n21 1.439; PrCOCH2C(OH)PrMe, PrCH(OH)CH2C(OH)PrMe, b15 110° (slow reaction); and iso-PrCOCH2C(OH)MePr-iso, -iso-PrCH(OH)CH2C(OH)MePr-iso, -, slower reaction than preceding because of greater hindrance. Distinction between intra- and intermol. H-bonding in a β-ketol was made on the basis of modifications of infrared spectra caused by (1) diln. with an inert solvent, and (2) admixt. with a compd. capable of assocn. with the ketol. p-ClC6H4OH was the most effective assocn. type indicator. Examn. of 14 β-ketols (primary, secondary, and tertiary) indicated intermol. assocn. Infrared analysis indicated reduction in intermol. assocn. of AcCHRCH(OH)Me as R increased from H to Me to Et, of AcCHRCH2OH as R increased from H to Et but little further change as R increased to Bu and Am, and of MeCR(OH)CH2COR as R increased from Me to iso-Pr. Dissocn. of AcCMe2CH2OH was much more important than that of the secondary ketols.

ACCESSION NUMBER: 1954:6997 CAPLUS
DOCUMENT NUMBER: 48:6997
ORIGINAL REFERENCE NO.: 48:1250g-i,1251a-h
TITLE: β-Hydroxy carbonylation and contribution to the study of steric effects
AUTHOR(S): Dubois, J. E.
SOURCE: Ann. chim. (Paris) (1951), 6, 406-86
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 49 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Chromones unsubstituted in the 2- and 3-position yield with CH2O and secondary amine HCl salts 3-(dialkylaminomethyl)chromone HCl salts (I); 2-methylchromones do not give this reaction. To 6.9 g. Na sand and 43.8 g. (CO2Et)2 in 100 cc. dry dioxane was added slowly with stirring 16.6 g. 2,5-HO(MeO)C6H3Ac in 50 cc. dioxane, the mixture stirred 2 hrs., 10 cc. EtOH and then 15 cc. AcOH added, the resulting stiff paste diluted with 900 cc. H2O, the solution extracted 24 hrs. with Et2O, the extract evaporated, the residue dissolved in 200 cc. Et2O, the Et2O solution washed with 80 cc. 10% NaHCO3 solution and two 50-cc. portions of H2O, dried, evaporated, the residue dissolved in 125 cc. EtOH and 125 cc. concentrated HCl, refluxed 1 hr., and the solution cooled and filtered to yield 10.4 g. (47%) 2-carboxy-6-methoxychromone, m. 268° (decomposition) (from EtOH), which, heated at about 350° until the CO2 evolution ceased and distilled, gave 5.1 g. (29%) 6-methoxychromone, m. 93-5° (from 50% aqueous EtOH). Similarly was prepared 2-carboxy-7-methoxychromone, decarboxylated at about 265°. A chromone (0.05 mole), 0.052 mole dialkylamine-HCl, 3 g. paraformaldehyde, and 16 cc. absolute EtOH refluxed 4-5 hrs. gave the I. By this method were prepared the following chromone-HCl's: 3-(dimethylaminomethyl) (II), 60%, m. 238-9°; di-Et analog, 7.5%, m. 167-8°; 3-(piperidinomethyl), 14%, m. 262-3°; and (morpholinomethyl), 20%, m. 244-6°. Similarly were prepared from the corresponding substituted chromones the following-substituted II (substituent given): 6-MeO (III), 22%, m. 234-6°; 7-MeO (IV), 47%, m. 235-6°; 6-Me, 21%, m. 230-1°; and 6-Cl, 46% m. 243-5°. Similar Mannich reactions with EtOCH:CHCOPh and EtOCMe:CHCOPh gave gummy, gelatinous nonbasic materials. Hydrogenation of 2 g. IV in 100 cc. 95% EtOH with 0.1 g. PtO2 at 50 lb./sq. in. gave 3-dimethylaminomethyl-7-methoxy-4-chromanone-HCl, m. 168-70°. 2-Methyl-6-methoxychromone (V) (5 g.) and 5 g. N-bromosuccinimide in 50 cc. CCl4 refluxed 3 hrs. with stirring gave 1.3 g. (17%) 2-bromomethyl-6-methoxychromone (VI), tan needles, m. 124-6° (from EtOH). VI (5.9 g.) and 2 g. Me2NH in 100 cc. EtOH heated 6 hrs. in a bomb with shaking at 95-105°, the EtOH evaporated, the residue taken up in 100 cc. H2O and 200 cc. Et2O, the mixture filtered and the Et2O layer dried and treated with dry HCl gave 0.05 g. III, m. 223°. To 12.5 g. V in boiling 600 cc. AcOH was added at once with stirring 2.35 g. MnO2 and 4.32 g. Br, the mixture refluxed 15 min. the cooled solution decanted from the unreacted MnO2, and the AcOH removed in vacuo to give 2-dibromomethyl-6-methylchromone, silvery crystals, m. 158.5-60° (from EtOH). A similar Mannich reaction on 5 g. 4-pyrone gave 2 g. of an unidentified, white, crystalline solid, m. 206°.

ACCESSION NUMBER: 1953:51550 CAPLUS
DOCUMENT NUMBER: 47:51550
ORIGINAL REFERENCE NO.: 47:8743i,8744a-e
TITLE: Chromones in the Mannich reaction
AUTHOR(S): Wiley, Paul F.
CORPORATE SOURCE: Lilly Research Labs., Indianapolis, IN
SOURCE: Journal of the American Chemical Society (1952), 74, 4326-8
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 50 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Compds. of the type RCOCR1(CH2NR2)CO2R3 (I), where R is alkyl or aryl and R1, R2, and R3 are the same or different alkyl radicals, are prepared by the condensation of RCOCHR1CO2R3 with HCHO and a secondary amine. The I are reduced to the corresponding alc. and esterified with an acid halide to yield products of the type RCH(OCOR4)CR1(CH2NR2)CO2R3, where R4 is an aryl radical. Cold aqueous 35% HCHO 22 is slowly added to a cold mixture of AcCHEtCO2Et 40 and Et2NH 18 g., the resulting mixture clarified with 50 cc. of MeOH, the product neutralized after 1 hr. with 40 g. of 25% HCl, extracted with Et2O, the aqueous layer treated with 70 g. of 30% aqueous KOH, and the alkaline solution extracted with Et2O; distillation of the extract yields Et α-(diethylamino-methyl)-α-ethylacetoacetate (II), b19 136-8°. Similarly are prepared Et α-diethylaminomethyl-α-methylacetoacetate, b19 129°; Et α-dimethylaminomethyl-α-ethylacetoacetate, b19 108-10°; Et α-dimethylaminomethyl-α-methylbenzoylacetate-HCl, m. 146-7°; and Et α-ethyl-α-(1-piperidylmethyl)-benzoylacetate-HCl, m. 144-5°. Reduction of II with 4 equivs. Al-Hg gives the unstable Et α-diethylaminomethyl-α-ethyl-β-hydroxybutyrate (III), b19 146°. III with R4COCl yields the corresponding Bz ester (IV), m. 33° (HCl salt, m. 138°); p-nitrobenzoyl ester-HCl, m. 161°. The latter on hydrogenation gives the p-aminobenzoyl ester (V), m. 194°; HCl salt, m. 198-9°. IV and V are local anesthetics.

ACCESSION NUMBER: 1953:3407 CAPLUS
DOCUMENT NUMBER: 47:3407
ORIGINAL REFERENCE NO.: 47:606e-h
TITLE: α-Dialkylaminomethyl-β-keto esters
PATENT ASSIGNEE(S): Luxema, Societe anon., Ste. Holding Luxembourgeoise
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 666590		19520213	GB	

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AB α-Substituted acroleins are prepared by passing a mixture of an aldehyde and HCHO into the molten salt of a primary or secondary amine. Into 7 moles Me2NH3Cl containing an emulsifying agent at 200° is slowly passed a 1.1:1.0 mixture of HCHO and PrCHO, N added during the reaction period, and the products condensed, washed, seph., and distilled to give 51% EtC(:CH2)CHO.

ACCESSION NUMBER: 1951:6295 CAPLUS
DOCUMENT NUMBER: 45:6295
ORIGINAL REFERENCE NO.: 45:1158i,1159a
TITLE: Acroleins
INVENTOR(S): Bortnick, Newman M.
PATENT ASSIGNEE(S): Rohm & Haas Co.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2518416		19500808	US	

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AB According to Mannich and Hof (C.A. 22, 590) EtAc and HCHO in the presence of Me2NH give a mixture of Me2NCH2CH2COEt (I) and AcCHMeCH2NMe2 (II), whereas, according to H., et al. (C.A. 39, 2334.8; 40, 6050.3), EtAc and HCHO in the presence of alkali or HCl give 3-condensation products. Repetition of M. and H.'s experiment shows that not I but AcC(CH2NMe2)2Me (III) is formed. This is proven by the fact that III requires 2 mols. HCl for neutralization, gives a pos. CHI3 test with NaOI in MeOH-KOH, a dipicrate, m. 106-8°, and a picrolonate, m. 184°. Refluxing 20 g. BzH and 70 g. EtAc 3 hrs. with 0.8 g. piperidine (IV), distilling off the EtAc, dissolving the residue in ether, washing the ether extract with HCl, and distilling the residue of the ether solution give PhCH:CHCOEt, b20 160-5°, m. 37°, gives a neg. CHI3 test. Refluxing 132 g. PhCH:CHCHO and 288 g. EtAc 6 hrs. with 5 g. IV and distillation of the reaction product give a fraction, b15 170-90°, from which is isolated 1.5 g. AcC(:CHCH:CHPh)Me, m. 69-70° (phenylhydrazone, m. 167-9°; semicarbazone, m. 225-7°). In the condensation of EtAc with aldehydes in the presence of secondary amines 1- as well as 3-condensation products may be formed, depending upon the structure of the aldehyde.

ACCESSION NUMBER: 1950:37940 CAPLUS
DOCUMENT NUMBER: 44:37940
ORIGINAL REFERENCE NO.: 44:7228f-i
TITLE: Condensation of butanone with aldehydes
AUTHOR(S): Haeussler, Herbert; Schacht, Wilhelm
CORPORATE SOURCE: Tech. Hochschule, Hannover, Germany
SOURCE: Chemische Berichte (1950), 83, 129-30
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 53 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Primary and secondary thenylamines and subresinous tertiary polythenylamines are obtained by treating thiophene (I) or its alkyl derivs. 1.5-3 hrs. at 65° or reflux temperature with either an NH4 halide and HCHO or hexamethylenetetramine and HCl. Primary and secondary amines can replace NH4Cl but (NH2CH2)2, urea, or thiourea do not give the corresponding products. I with aqueous HCHO and NH4Cl gives 2-thenylamine (II), di-2-thenylamine (III), and a polymeric amine (IV) containing the grouping -CH2N(CH2OH)CH2- or HOCH2(C4H2S)CH2N-, which on heating liberates H2O and forms resinous products. Tabulated data on the effect of the mol. ratios of reactants on the reaction products indicate that an excess of I or NH4Cl minimizes the formation of IV and that IV is formed from the secondary amine since the yield of the 2 compds. varies in inverse proportion. For high yields of primary and secondary amines at least 2 mols. NH4Cl/mol. I should be used. The utilization of I, aqueous HCHO, and NH4Cl appears to be independent of the mol. ratio of the reactants and is 1:2:1, but the mol. weight of IV varies with the mol. ratio of the reactants. NH4Cl 1.03, I 2.0, and HCHO (in the form of 37% aqueous HCHO) 1.23 mols. were heated 3 hrs. at 74°, the unreacted I decanted, EtOH added to the reaction mixture which was then filtered, freed from EtOH by evaporation, the residue neutralized with KOH solution, extracted with C6H6, the solvent removed, and the residue distilled in vacuo to give 9 g. II, b5 55-65°, nD20 1.5650, 8 g. III, b7 115-45°, nD20 1.5914, and 25 g. residue; the properties of several derivs. of II are listed. I 2, hexamethylenetetramine 0.5, and aqueous HCl 2 mols. were kept 45 min. at 76-80°, I removed by distillation, and the mixture worked up as before, yielding II 33.0 and III 16 g. Bu2NH 1, concentrated HCl 1, I 1, and HCHO 1 mol. heated 6 hrs. at 80° gave after neutralization a product, b. 298-308°, containing 21.3% S and 8.67% N. No reaction took place on heating I with paraformaldehyde and NH4Cl but formation of II, III, and IV occurred after addition of AcOH to the reaction mixture, demonstrating the need for a depolymerizing agent for paraformaldehyde. Further examples are given which show the effect of the mol. ratio of the reactants on the production of IV. The main uses for II and III are as bearing-corrosion inhibitors for engine lubricants, but they are also suitable as intermediates for the manufacture of dyes, pharmaceuticals, or as insecticides.

ACCESSION NUMBER: 1950:22717 CAPLUS
DOCUMENT NUMBER: 44:22717
ORIGINAL REFERENCE NO.: 44:4509g-i,4510a-d
TITLE: Thenylamines
INVENTOR(S): Hartough, Howard D.; Lukasiewicz, Sigmund J.
PATENT ASSIGNEE(S): Socony-Vacuum Oil Co., Inc.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2497067		19500214	US	

L19 ANSWER 54 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

oil; this is also the final product of decompn. of VII, VIII, and X. On standing XIII evolves NH3 and gives the compd., C5H12O3N2 (XIV), m. 98°; it does not contain primary or secondary NO2 groups; with alkali it gives NH3, and with concd. EtOH-HCl, HCHO and the HCl salt of XIII result; the mother liquor from XIV yields 10% (on basis of XIII) of a strongly alk. oil (piperidine odor), C10H20O4N4, b16 160°, nD22 1.4862; it does not form a cryst. picrate or methiodide. III in concd. HCl, evapd. to a sirup, yields the HCl salts of V, IX, XI, and the HCl salt of HOCH2CEt(NO2)CH2NHCH2OH, sepd. by crystn. from EtOH and ether. IX was not obtained from IV.

ACCESSION NUMBER: 1948:778 CAPLUS
DOCUMENT NUMBER: 42:778
ORIGINAL REFERENCE NO.: 42:175a-i,176a-b
TITLE: Reaction of 1-nitropropane with formaldehyde and ammonia
AUTHOR(S): Hirst, E. L.; Jones, J. K. N.; Minahan, S.; Ochynski, F. W.; Thomas, A. T.; Urbanski, T.
CORPORATE SOURCE: Royal Arsenal, Woolwich, UK
SOURCE: Journal of the Chemical Society, Abstracts (1947) 924-8
CODEN: JCSAAZ; ISSN: 0590-9791
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 54 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

GI For diagram(s), see printed CA Issue.

AB PrNO2 (89 g.) in 225 cc. 40% HCHO and 59 cc. 33% NH4OH, stirred 12-15 hrs. at room temperature, gives an oily precipitate containing EtCH(NO2)CH2OH; addition of NaCl to the aqueous solution gives 100 g. of the additive compound, (C5H11O4N)3.C6H12N4 (I), of HOCH2CEt(NO2)CH2OH (II) and (CH2)6N4, m. 117°; I results also (4.2 g.) from 4.47 g. II and 1.4 g. (CH2)6N4 in concentrated aqueous solution; it is dissociated in solution; on heating it forms a resin. PrNO2 (89 g.), 225 cc. 40% HCHO, and 59 cc. 33% NH4OH, stirred 15-30 min. at 90-5°, the product poured onto ice, and the oily layer reheated 8 hrs. at 90-5°, give 110-25 g. of resin A (III); similarly, 149 g. II gives 110 g. of resin B (IV), a colorless and odorless viscous liquid. Distillation of III and IV under reduced pressure gives EtCH(NO2)CH2OH, an unidentified blue NO derivative, and fractions b0.01 140°, nD16 1.4720, and b0.01 160-80°, nD16 1.4880; these contain 5-nitro-5-ethyltetrahydro-1,3-oxazine (V), H2C.NH.CH2.O.CH2.CEtNO2, nD18 1.4873 (HCl salt, m. 203° (decomposition); picrate, pale yellow, m. 156°). V and MeI give 5-nitro-3-methyl-5-ethyltetrahydro-1,3-oxazine-MeI (VI), m. 218° (decomposition); VI results also from III or IV and MeI; picrate m. 210°. VI with Ag2O yields the hydroxide which decompose violently on distillation, giving Me2NH (identified as the picrate), a 2nd base which with MeI yields a derivative m. above 300°, and an aldehyde or ketone whose 2,4-dinitrophenylhydrazone, C11H14O4N4, m. 166°. Steam distillation of 9.3 g. III or IV yields 6 g. of an oil (mainly V); extraction of the aqueous distillate with ether and C6H6 gives 5-nitro-5-ethyl-3-(2-nitro-2-(hydroxymethyl)butyl]tetrahydro-1,3-oxazine (VII), H2C.CEt(NO2).CH2.O.CH2.NCH2C(NO2)EtCH2OH, m. 101°. PrNO2 (89 g.), 225 cc. 40% HCHO, and 59 cc. 33% NH4OH, heated 1.5 hrs. at 90-5°, give 15-20 g. 5,7-dinitro-3-(hydroxymethyl)-5,7-diethyl-1-oxa-3-azacyclooctane (VIII), O2NEtC.CH2.N(CH2OH).CH2.O.CH2.CEtNO2.CH2, m. 97°; cold concentrated HCl gives the HCl salt, m. 174°, which is hydrolyzed by cold H2O. VIII, warmed with concentrated HCl, loses 1 mole HCHO and yields the HCl salt (IX), m. 197°, of N-(hydroxymethyl)-2,4-dinitro-4-(hydroxymethyl)-2-ethylhexylamine, HOCH2C(NO2)EtCH2C(NO2)EtCH2NHCH2OH (X), an oil. IX, heated with aqueous HCHO, yields VIII. With NaNO2 IX gives an oily NO derivative which regenerates IX with concentrated EtOH-HCl. The picrate of X, pale yellow, m. 154°, could not be crystallized from H2O. Distillation of X yields V and EtCH(NO2)CH2OH. II (149 g.), 75 cc. 40% HCHO, and 26 cc. 33% NH4OH, heated 1.5 hrs. at 95-6°, give 50 g. VII; it can be prepared from IV by solution in cold concentrated HCl, pouring onto ice, and extracting the resinous precipitate with ether. With cold concentrated HCl, VII yields the HCl salt, m. 156°; it results also by passing HCl through VII in CHCl3 or CCl4; it is hydrolyzed by H2O. VII (or its HCl salt), heated with concentrated HCl, loses 1 mole HCHO and is converted to the HCl salt (XI), m. 186°, of bis[2-nitro-2-(hydroxymethyl)butyl]amine (XII), NH[CH2CEt(NO2)CH2OH]2, m. 54° (picrate, m. 148°). XI and aqueous HCHO give VII. The oily NO derivative regenerates XI with concentrated HCl. On boiling XII in H2O 2 moles HCHO are liberated. Distillation of XII gives V, EtCH(NO2)CH2OH, and unchanged XII. The HCl salt of V, boiled with H2O, gives 1 mole HCHO and the HCl salt, m. 126°, of 2-nitro-2-(hydroxymethyl)butylamine (XIII), an

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AB An investigation is reported of the manner in which the hydroxyphenyl group of tyrosine (I) might react with HCHO, as well as the stability to acid hydrolysis of any linkages that might be thus formed. I (80 g.) in 323 cc. 2.74 N NaOH was treated with 26.6 g. HCHO and the mixture kept at 20° for 10 days; the filtrate was adjusted to pH 5.5 with HCl and the precipitate was purified by solution in N NaOH and precipitation at pH 5.5. The optical rotation of the solution (followed for 40 days) and the decrease in free HCHO indicate that 1 mol. of HCHO is taken up rapidly and a 2nd mol. much more slowly. The reaction product (II), (C11H13NO4)x, is amorphous, [α]D25 18.1° (3 N NaOH, c 0.9), solubility in H2O 0.01%, more readily soluble in alkali than in acid. Air-dried II heated at 105° continues to lose weight slowly. X-ray diffraction patterns of II indicated its amorphous nature. The absorption maximum of II is at 284 m., sp. extinction coefficient 9.81. Electrophoretic patterns of II in barbital buffer at pH 7.8 show 2 definite peaks; heterogeneity of II was substantiated by fractionation of an alkaline solution with dilute acid; although the larger portion precipitated at pH 5.5, small fractions were obtained at pH 4.5 and 3.5. Dialysis of II against distilled H2O for 6 days yielded none of the material in the dialyzate. Hydrolysis of II with N acid for 7 hrs. liberated no HCHO. II contains no amino N; that the N of II is secondary rather than tertiary was shown by the fact that addition of HCHO to an aqueous alkaline solution caused a drop in pH. When heated at 105°, II becomes less soluble in 0.1 N NaOH but is not resinified. When heated with catalytic quantities of NaOH or NH3, II gives light-brown, transparent, somewhat brittle resins; HCl gives a tough, opaque resin. Acetylation of II gives products containing 4.7 to 5.9% N. Inorg. salts, picrates, and methylated derivs. do not have constant compns.

ACCESSION NUMBER: 1946:24996 CAPLUS
DOCUMENT NUMBER: 40:24996
ORIGINAL REFERENCE NO.: 40:4911a-e
TITLE: Polymer reaction product of tyrosine and formaldehyde
AUTHOR(S): Brown, Alfred E.
CORPORATE SOURCE: Eastern Regional Research Lab., Philadelphia
SOURCE: Journal of the American Chemical Society (1946), 68, 1011-15
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB A secondary aliphatic alc. 2 mols. are refluxed with CH2O (as aqueous solution or paraformaldehyde) 1-20 mols. and a strong acid 3-50% until at least 10% of a H2O-insol. condensation product is formed, boiling at least 20° above the corresponding formal and having a d. at least 3% greater. Thus refluxing sec. C7H15OH 116, 40% aqueous CH2O 85 and 47% H2SO4, 40 parts for 1 hr., separating and drying the nonaq. layer, and distg . gave 140 parts of product, 2/3 of which boiled 150-260°. Some of the products are nitrocellulose solvents.

ACCESSION NUMBER: 1946:7743 CAPLUS
DOCUMENT NUMBER: 40:7743
ORIGINAL REFERENCE NO.: 40:1354h-i
TITLE: Reaction products of secondary aliphatic alcohols and formaldehyde
INVENTOR(S): Harvey, Mortimer T.
PATENT ASSIGNEE(S): Harvel Research Corp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2388409		19451106	US	

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AB cf. C.A. 39, 1889.3. This work was undertaken when it was observed that gliadin and wheat gluten bound more HCHO than did other proteins after treatment with 4% HCHO at 70° and pH 3-7. It was possible to demonstrate that the primary amide as well as the NH2 groups of proteins bound aldehyde under these conditions. The secondary amides of the peptide chain did not react appreciably with HCHO. In most expts. 1 g. of protein or polypeptide in 8 ml. of H2O was treated with 1 ml. of buffer and 1 ml. of 37-8% HCHO and kept at 70° for 4 days (intermittent shaking); the aldehyde contents of the final products varied by no more than 10% with the different techniques of isolation. Of the final amount of HCHO, 50% was bound in 8 hrs. and 90% in 24 hrs. Lysozyme bound about 37% more HCHO at pH 6.8 than at pH 3.8; egg-white protein 18% more, gluten 10% more, zein the same amount at both pH levels, and polyglutamine 38% less at the higher pH. The HCHO concentration and the reaction temperature affect the maximum amount of HCHO introduced; gluten bound about 2% of its weight of HCHO when treated at room temperature with 3.8% HCHO or at 70° with 0.75% HCHO; the use of 18% HCHO at 70° (pH 3.8) introduced 7% of HCHO as compared with 6% from 3.8% HCHO. The HCHO retained by the proteins after the usual washing procedure was comparatively stable during further prolonged contact with H2O at room temperature Steam distillation caused the release of most of the bound HCHO. Heating the dry material at 100° for 7 days reduced the HCHO content by 60-70%; at 150° for 3 days, by 85%. Exhaustive washing of aldehyde-treated proteins with Na2SO3 is not a suitable technique for removal of unbound HCHO. Details are given of the preparation of polyglutamic acid, its Me ester, and polyglutamine. The moles of aldehyde bound at pH 3.5-4 and 70° per 104 g. of protein, etc. (values are given also for primary NH2, total basic, and primary amide groups) are: polyglutamine 47, gliadin 23 (PhNCO-treated, 9), gluten 20 (HNO2-treated 4, PhNCO-treated 5), lysozyme 13, zein 15 (HNO2-treated 8), casein 12 (HNO2-treated 6), hoof powder 12, egg-white protein 11 (PhNCO-treated 4), egg albumin 9, wool keratin 11, feather keratin 8, gelatin 6, polyglycine 3, polyglutamic acid 2.6, silk fibroin 2.3, nylon 0.3. The amino-N contents of the treated proteins were reduced to 10-20% of the starting materials. There is a correlation between the sum of the basic and the amide groups of proteins and their capacity to bind HCHO; thus, these groups are responsible for a great part of the HCHO bound by proteins under the conditions used.

ACCESSION NUMBER: 1945:20833 CAPLUS
DOCUMENT NUMBER: 39:20833
ORIGINAL REFERENCE NO.: 39:3315i,3316a-f
TITLE: Reaction of CH2O with proteins
AUTHOR(S): Fraenkel-Conrat, Heinz L.; Cooper, Mitzi; Olcott, Harold S.
SOURCE: Journal of the American Chemical Society (1945), 67, 950-4
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 58 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
GI For diagram(s), see printed CA Issue.
AB Unlike secondary amines, primary amines, such as MeNH2, react only poorly with HCHO and ketones to form 1,3-keto bases with a secondary N atom, and only with special ketones like Et2CO or MeCOPh (Mannich and Heilner, C. A. 16, 2497). With PhCH2NH2.HCl (or 3,4-CH2O2C6H3CH2NH2), however, there is obtained with HCHO and ketones, such as cyclohexanone (I), acetone, PhCH:CHCOMe, 1-tetralone, PhCOMe and cyclopentanone, up to 65% of the corresponding keto bases: PhCH2NH2.HCl + HCHO + RCH2COR' → H2O + PhCH2NHCH2CHRCOR'.HCl. In these 1,3-keto bases, unlike the 1,3-amino alcs. obtained by their reduction, the PhCH2NH residue is loosely held. In the hydrogenation of II under pressure and at elevated temps. PhCH2NH2 is often formed along with the alc. base. As byproducts in the preparation of 1,3-keto bases there are also formed tertiary bases when a double amount of HCHO is used; they are also formed from 1 mol. PhCH2NH2, 2 mols. HCHO and 2 mols. ketone, "ketol condensation" occurring with formation of a piperidine or isoquinoline ring. The tertiary base obtained by M. and Heilner from MeNH2, CH2O and PhCOMe is likewise to be regarded as a keto alc. base, not as a diketo base; its reduction product is not a pinacol but a secondary-tertiary glycol. Some of the products obtained are alkaloid-like, such as 2-benzyl-4-acetyl-10-hydroxydecahydroisoquinoline or 2-(3,4-methylenedioxybenzyl)-4-acetyl-10-hydroxydecahydroisoquinoline, and possess, along with low toxicity, spasmolytic properties; the latter of the 2 compds. is half as effective as papaverine. Attempts to use, instead of ketones, appropriate aldehydes (e. g., iso-PrCHO) are being made. 2-(Benzylaminomethyl)cyclohexanone (II): 36 g. PhCH2NH2.HCl (III), 20 g. of 40% HCHO (IV) and 74 g. I were heated and, after the reaction had subsided, were again brought to a boil, 5 g. IV was added to bind unreacted III, the excess of I distilled off, the residue dissolved in 100 cc. water, the solution made alkaline after extraction with ether, again extracted with ether, the extract shaken out with just enough 20% HBr, the salt solution concentrated somewhat in vacuo, the HBr salt of the tertiary amine (V), m. 186° (about 10% yield) separated, the filtrate evaporated and the residue crystallized from AcOEt. The HBr salt of II m. 129° (65% yield); oxime, needles, m. 85°; N-Bz derivative, m. 134°. N-Carbethoxy derivative, from the free II and ClCO2Et in pyridine, oil with bitter taste, b11 222°. 2-(Benzylaminomethyl)cyclohexanol, from III in water kept acid with HCl and Na-Hg, precipitated with KOH and distilled in vacuo, b16 194-7°. After neutralization with HBr there seps. the α-form of the HBr salt, m. 160-1° (from acetone), while the β-form, after separation of the α-HBr salt, is precipitated as the free base, distilled and isolated as the HCl salt, m. 144°. HCl salt of the α-form, m. 160°. Bz derivative of α-form, m. 159-60°; of β-form, m. 148°. 2-Oxo-3-benzyloctahydroquinazoline, from II.HBr with KCNO by spontaneous cleavage of water from the intermediate, nonisolable urea derivative, m. 191° (from alc. or AcOEt). It is disproportionated by boiling 20% HCl; on concentration and addition of water 2-oxo-3-benzyldecahydroquinazoline, m. 175° (from alc.), ppts. and evaporation of the filtrate yields the HCl salt of the hexahydro compound, yellow needles from 25% acetone, m. 212°; free base, m. 153°. The tertiary base V is also obtained in up to 25% yield from III, IV and I in the mol. ratio 1:2:1. After separation of II as the quinazoline with KCNO, V

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is pptd. with KOH and crystd. from MeOH; free base, m. 102°; HBr salt, m. 186°; HCl salt, m. 176°; oxime, m. 186°. With Na-Hg in dil. AcOH V gives the diHO base, m. 162° (from MeOH); diacetate, m. 154° (from MeOH). 2-Benzyl-4-acetyl-10-hydroxydecahydroisoquinoline (VI): After 5 h. boiling of 12 g. II.HBr, 1.2 g. paraformaldehyde, 50 cc. acetone and a few drops of HCl (mixt. acid to Congo) and 3 h. boiling after addn. of another 1.2 g. paraformaldehyde, distn. of the acetone, and addn. of 40 cc. water, ice-cold KOH ppts. 8 g. VI, m. 96° (from petr. ether); HCl salt, m. 195°; oxime, m. 131°. 2-Benzyl-4-(1-hydroxyethyl)-10-hydroxydecahydroisoquinoline was obtained from VI by hydrogenation with Pt oxide in alc. as the HCl salt, m. 240-1° (from abs. alc.); free base, needles, m. 115-17° (from petr. ether). 2-Benzyl-4-acetyloctahydroisoquinoline: The tertiary HO group of VI is split off as water with concd. H2SO4; the cleavage may occur in different directions. The mixt. from 2 cc. concd. H2SO4 and 1 g. VI was poured after 3 days into NaOH, the free base extd. with ether, the ether neutralized with HClO4, the residue from the ether treated with alc. and cooled with ice; after sepn. of 0.2 g. perchlorate A (m. 146°) the residue was dissolved in hot water; cooling gave 0.1 g. perchlorate B, m. 201°. Hydrogenation of the free bases from perchlorates A and B in alc. with Pt oxide gave 2-benzyl-4-acetyldecahydroisoquinoline; acid oxalate, m. 156°. 2-Benzyl-4-benzoyl-10-hydroxydecahydroisoquinoline (VII), obtained as the HCl salt with 1 mol. H2O from II by heating with ClCH2CH2COPh in alc. (yield, 50%), m. 212°; free base, m. 164° (from ligroin). VII is also obtained from PhCH2NH2.HBr, MeCOPh and IV in dioxane. 2-Benzyl-4-benzoyloctahydroisoquinoline, obtained from VII treated with concd. H2SO4, poured into NaOH and extd. with ether, tables, m. 97° (from alc.). 1-Benzylamino-3-oxobutane (VIII), obtained as the HCl salt from III (soln. acid to Congo), paraformaldehyde and acetone by boiling, distn. and recrystn. of the residue from acetone, leaflets, m. 162°; HBr salt, m. 124-6° (from acetone); free base, b6 155°; oxime 0 HCl salt, needles from water, m. 151°; urea deriv., from the HCl salt with concd. KCNO, white needles, m. 120-1° (from MeOH). 1-Benzylamino-3-hydroxybutane (IX), b2 122-3°, was obtained by redn. of VIII in weakly acid soln. with Na-Hg, pptn. with KOH and distn.; HBr salt, m. 57° (from acetone). p-O2NC6H4COCl in CHCl3 with VIII gives a mixt. of the N-p-nitrobenzoyl compd., pale yellow leaflets, m. 236°, and the corresponding HCl salt, white leaflets, m. 191°. 1-Benzylamino-3-bromobutane was obtained in 18 g. yield, and from 15 g. IX and 75 g. of 66% HBr heated 8 h. in a tube at 160° and treated with water, as the HBr salt, colorless needles, m. 212° (from acetone). The free base did not condense with CHNa(CO2Et)2 but split off HBr with formation of 1-benzylamino-2-butene, b12 95°. HCl salt, white leaflets, m. 134-5°. The base was hydrogenated to PhCH2NHBu; HCl salt, m. 242°. 1-Benzyl-4-hydroxy-4-methyl-5-acetylpiperidine (X): From 70 g. VIII.-HCl, 20 g. paraformaldehyde and 450 cc. acetone there was obtained, after boiling 10 h., distg. off the acetone, taking up in 1.5 l. water and pptg. with KOH, a thick oil, probably the stereoisomeric forms of X, which after redn. with Na-Hg yielded a mixt. of the 2 forms of 1-benzyl-4-hydroxy-4-methyl-5-(1-hydroxyethyl)piperidine, b12 220-5°; from this was isolated 20% of a perchlorate m. 201°; the free base from the latter b12 223° and formed a HBr salt, m. 175°, (from acetone), and a di-Ac deriv., needles, m. 129-31°. 1-Benzylamino-4-benzylidene-3-butanone (XI): Equimol. amts. of III, IV and PhCH:CHCOMe yielded, after heating, 20% of the HCl salt of XI, m. 182-4°, difficultly sol. in acetone, and, after distn. of

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the acetone, treatment with KOH, extn. with ether and evapn. of the ether, 5-10% of 1-benzyl-4-hydroxy-4-styryl-5-cinnamoylpiperidine, pale yellow needles, m. 148° (from acetone). The free XI m. 50-1° (from petr. ether) and changes on standing into an acid-insol. red-brown resin. Hydrogenation of XI.HCl with Pt oxide in MeOH gives the HCl salt of 1-benzylamino-4-benzyl-3-butanol, m. 99-100°; free base, small needles, m. 87-9° (from ligroin). 3-(Benzylaminomethyl)-4-oxotetralin (XII) was obtained by heating equimol. amts. of 1-tetralone, III and IV as the HCl salt (yield, 55%), m. about 160° (from alc.-acetone), gives with KCNO through the nonisolable urea deriv. a pyrimidine deriv., slender gleaming leaflets, m. 208° (from alc.). With NaNO2 in HCl, XII.HCl gave 90% of the nitrosamine, needles, m. 94°, yielding on boiling with Sn and concd. HCl 2-benzyltetrahydro-6,7-benzindazole as the HCl salt, m. 173° (from acetone). β-(Benzylamino)propiophenone (XIII): III (9 g.), 5 g. IV and 8 g. MeCOPh were boiled and, after distg. off the water formed, were taken up in acetone. The difficultly sol. HCl salt of XIII (9.5 g.), needles, m. 163°; free base, leaflets, m. 67° (from petr. ether). With concd. KCNO the HCl salt gives 1-benzyl-1-(2-benzoylethyl)urea, needles, m. 131° (from iso-PrOH). 1-Benzyl-4-hydroxy-4-phenyl-5-benzoylpiperidine (XIV): From the oily residue from the acetone mother liquors in the prepn. of XIII were pptd. the basic constituents, which in dil. HCl with KCNO gave XIV, m. 116°. 2-(Benzylaminomethyl)-cyclopentanone (XV), from III, IV and cyclopentanone, needles, m. 157° (from abs. alc.; a byproduct remains undissolved). Urea deriv. of XV, needles, m. 126-7° (from iso-PrOH). (3,4-Methylenedioxybenzyl) (2-oxo-cyclohexylmethyl)amine (XVI) was prepd. from 3,4-CH2O2C6H3CH2NH2.HCl (XVII) like II. The soln. of the HBr salt yielded 2 salts sepd. by hot abs. alc.: the sol. salt of the secondary base (XVI), m. 155-6°, and the slightly sol. salt of the tertiary base (5% yield), m. 250°. N-Bz deriv. of XVI, needles, m. 118°. 2-Oxo-3-(3,4-methylenedioxybenzyl)octahydroquinazoline, from XVI.HCl with KCNO, needles, m. 168°. The base corresponding to V, from IV, XVII and I, forms needles, m. 167° (from MeOH). 2-(3,4-Methylenedioxybenzyl)-4-acetyl-10-decahydroisoquinoline, from XVI.HBr, paraformaldehyde and acetone, needles, m. 127° (from MeOH). 1-(3,4-Methylenedioxybenzylamino)-3-oxobutane was prepd. from XVII like VIII; HCl salt, m. 176°. 3-[(3,4-Methylenedioxybenzylamino)methyl]-4-oxotetralin was prepd. like XII; HCl salt, m. 186°. With KCNO it gives 2-oxo-3-(3,4-methylenedioxybenzyl)naphthopyrimidine, fine needles, m. 228°. β-(3,4-Methylenedioxybenzylamino)propiophenone was prepd. like XIII; HCl salt, m. 187°; urea deriv., m. 144°. 1-(3,4-Methylenedioxybenzylamino)-4-benzylidene-3-butanone was obtained like XI; HCl salt, m. about 186°. Hydrogenation with Pt oxide gives the HCl salt of 1-(3,4-methylenedioxybenzylamino)-4-benzyl-3-butanone, m. 205°. 2-[(3,4-Methylenedioxybenzylamino)methyl]cyclopentanone, analogous to XV, needles, m. 161-2°; urea deriv., m. 160°. Benzyl(benzylamino)(2-oxocyclohexyl)-methane (XVIII): A mixt. of 2.1 g. PhCH2NH2 and 2.4 g. PhCH2CHO is treated, after drying with K2CO3, with 6 g. I, satd. in ice, after 1 day, with HCl gas, treated after 15 days with water and extd. with ether; the ether yields 0.3 g. XVIII as the HCl salt, m. 154°.

ACCESSION NUMBER: 1943:6655 CAPLUS
DOCUMENT NUMBER: 37:6655
ORIGINAL REFERENCE NO.: 37:1125b-i,1126a-i,1127a-h
TITLE: Synthesis and reactions of 1,3-ketonic bases with secondary nitrogen
AUTHOR(S): Mannich, Carl; Hieronimus, Otto

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SOURCE: Ber. (1942), 75B, 49-64
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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GI For diagram(s), see printed CA Issue.

AB The object of this work was to apply the Tollens' reaction (Ann. 289, 46 (1896)) between HCHO and ketones in the presence of Ca(OH)2 to p-amino ketones for the preparation of aminohydroxy ketones and aminopolyhydroxy compds. It seemed advisable to use an amino ketone with tertiary N to avoid the complications which might arise from the reaction of the HCHO with a primary or secondary amino group, and hence the readily available MeCOCH2CH2NMe2 (I) (C. A. 12, 684) was selected. Aqueous I reacts readily with HCHO without addition of Ca(OH)2 being necessary; the alkalinity of the I itself is sufficient. At 0° 1 mol. HCHO is to a great extent, but not completely, used up in the course of several hrs., and from the reaction mixture there can be isolated some unchanged I, a diamine, MeCOCH(CH2NMe2)2 (II), and a further basic fraction (III). The formation of II shows that I partially breaks down with liberation of NHMe2. All attempts to establish the nature of III, which presumably contained the dimethylaminohydroxy ketones sought, resulted in resinification or decomposition. Accordingly, as 1,3-amino ketones are known to be sensitive whereas the corresponding alcs. are stable, recourse was had to reduction. When a mixture of I, water and 1 mol. HCHO is acidified with HCl after some hrs. and reduced with Na-Hg there is obtained a mixture of bases which can be separated by fractional distillation into about equal parts of (1) 1-dimethylamino-3-butanol (IV), b12 55-65°, and (2) 1-dimethylamino-2-(dimethylaminomethyl)-3-butanol (V), b12 85-100°, (3) a mixture, b12 130-45°, of diastereomeric α- and β-1-dimethylamino-2-hydroxymethyl-3-butanols (VI), and (4) a thick oil, b12 180-200°, probably a mixture of dimethylaminotrihydroxyhexanes (VII), HOCH2CH2CH(OH)CH(CH2OH)CH2NMe2, one of which was isolated as a methiodide. The formation of the stereomeric VI shows that the original condensation product contained the corresponding HO ketone which, on reduction, gives 2 glycol bases because an addnl. asym. C atom is produced. Possibly a ketone, HOCH2CH2COCH2CH2NMe2, is also formed in small amount but the corresponding reduction product was not found. Separation of the 2 VI is difficult. α-VI can be isolated as the dibenzoate-HBr and obtained pure by saponification of this ester. The 2 HO groups can readily be replaced by Cl; the resulting α-1-dimethylamino-2-chloromethyl-3-chlorobutane (VIII) gives with MeNH2 the triamine, MeCH(NMe2)CH(CH2NMe2)2 (IX) (see following abstract), b12 91°. β-VI has not as yet been obtained pure, but the di-Cl compound, β-VIII, has; the latter with NHMe2 gives the same IX as does α-VIII. α- and β-VIII by ring closure give the same quaternary dimethyl(β-1-chloroethyltrimethylene)ammonium chloride, Me2Cl (X), which establishes the structure MeCHClCH(CH2Cl)CH2NMe2 of the VIII, for a compound of the structure ClCH2CH2CHClCH2CH2NMe2, which would yield a piperidinium salt on ring closure, could not exist in 2 stereomeric forms. Moreover, that X is a trimethyleneimonium salt is shown by its behavior on thermal decomposition; the ring is opened and a mixture of α- and β-VIII distils over, whereas a piperidinium salt would give MeCl and a monochloropiperidine. Fraction (4) above has a composition corresponding approx., but not exactly, to VII; Zerevitinov detns. show 3 mobile H atoms and acetylation with Ac2O gives an oil (XI) with an AcO content agreeing with that of a triacetate; from both VII and XI, which are undoubtedly mixts. of isomers, can be isolated about 30% of homogeneous methiodides which are genetically related, for the methiodide obtained from XI gives on cautious saponification that obtained from VII.

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Hofmann degrdn., VII.MeI splits off 1 mol. NMe3 and gives a high-boiling, N-free, H2O-sol., thick, very hygroscopic liq. unsatd. toward KMnO4. α-VI, b12 133-5°; HI salt, m. 113°; methiodide, m. 115°; dibenzoate-HBr (XII), m. 224°. α-VIII.HCl, from α-VI and SOCl2 in CHCl3, m. 165°; free VIII, b12 80°; HBr salt, m. 164°. The mother liquors from XII, on sapon., give a mixt. of α- and β-VI in which, however, the β-form has been so concd. that it can be isolated as the methiodide, m. 140°. With SOCl2 in CHCl3, 9 g. of this mixt. yields about 3 g. α-VIII.HCl and 7 g. β-VIII.HCl, m. 129-31°, which gives the free β-VIII, b11 78°, whose HBr salt m. 148-9°. X, from α-VIII and NaI in acetone allowed to stand 8 days at room temp. or from β-VIII.HCl and KOH in ether heated 14 days at 50°, is isolated as the chloroaurate, yellow, m. 133°; the hygroscopic chloride, cautiously heated in vacuo, regenerates a mixt. of α- and β-VIII. 1-Dimethylamino-2-methylene-3-chlorobutane, from X shaken with Ag2O, filtered, evapd. in vacuo and heated higher, b46 86°; HCl salt, m. 179°, decolorizes aq. KMnO4 and Br. (2-Hydroxymethyl-3,5-dihydroxyamyl)trimethylammonium iodide, VII.MeI, m. 114°. XI, b15 185°; methiodide, m. 173-4°.

ACCESSION NUMBER: 1939:29734 CAPLUS
DOCUMENT NUMBER: 33:29734
ORIGINAL REFERENCE NO.: 33:4195c-i,4196a-e
TITLE: Dimethylaminodihydroxypentanes and dimethylaminotrihydroxyhexanes
AUTHOR(S): Mannich, Carl; Salzmann, Otto
SOURCE: Ber. (1939), 72B, 499-505
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB cf. C. A. 31, 2591.1. Condensation of phenolic ethers with HCHO and HCl in the presence or absence of dehydrating catalysts gives, under favorable conditions, the corresponding chloromethyl derivs. which can be converted, by treatment with NaOAc in AcOH and saponification of the resulting acetic esters by KOH in dilute alc., into methoxybenzyl alcs. This method has been applied to the Me ethers of the cresols, thymol and to nitronisole to prepare the corresponding benzyl alcs. A well-cooled mixture of 244 g. of o-MeC6H4OMe and 180 g. of 40% HCHO was saturated, with stirring below 5°, with a rapid current of HCl. The reaction product was treated with ice and extracted with petr. ether. The extract was washed, dried over Na2SO4 and evaporated Rapid distillation gave the chloromethyl compound, 3-methyl-4-methoxybenzyl chloride, b20, 119°, d420 1.130, nD20 1.548, decomposing on heating. The crude product was therefore poured into a warm solution of 164 g. anhydrous NaOAc in 400 g. AcOH, evaporated free from petr. ether and heated for 30 min. at about 100°. The crude ester was extracted with Et2O and saponified by boiling for 1 hr. with 100 g. KOH in 200 g. of 95% alc. and 200 g. H2O. The solvents were evaporated off in vacuo and the crude alc. was extracted with Et2O and fractionated, yielding 40% (125 g.) of 3-methyl4-methoxybenzyl alc., b18 148-9°, d416 1.095, nD16 1.5445; phenylurethan, m. 90.5°, and 74 g. of 3,3'-dimethyl-4,4'-dimethoxydiphenylmethane (cf. R. Quelet, C. A. 28, 2687.1), b7 193-4°, m. 24°, formed as a secondary product in the chloromethylation of o-MeC6H4OMe. Similar treatment of 183 g. of m-MeC6H4OMe, b. 174-5°, nD20 1.5140, gave 140 g. of crude product which, on fractional distillation, yielded 15% (30 g.) of 2-methyl-4-methoxybenzyl alc., b18 145°, nD18 1.5455 (oxidized by KMnO4 to 2-methyl-4-methoxybenzoic acid, m. 176°, and forming a phenylurethan, m. 71°), and 80 g. of 2,2'-dimethyl-4,4,'-dimethoxydiphenylmethane, m. 69°, oxidized by CrO3 to the corresponding henzophenone, m. 72°. The poor yield of alc. is due to the instability of the chloromethylintermediate which tends to condense with the Me cresolate to give the di-Ph derivative and with itself to form resins. A well-stirred mixture of p-MeC6H4OMe, 150 g. of 40% HCHO and 60 g. ZnCl2 was saturated with HCl at 25° for 75 min. The product was washed with H2O, shaken with dilute NaOH, rewashed, dried over Na2SO4 and immediately distilled, yielding 295 g. of 2-methoxy-5-methyl-α-chlorotoluene, b16 124°, d416 1.128, nD16 1.5455, transformed by heating for 1 hr. at 100° with a slight excess of NaOAc in AcOH into the Ac derivative, C11H14O3, b16 146°, d416 1.091, nD16 1.515, which was saponified in 80% yield to 2-methoxy-5-methylbenzyl alc. C9H12O2, b16 140-1° d416 1.092, nD16 1.5427 (phenylurethan, m. 90°), oxidized by KMnO4 in the cold to 2-methoxy-5-methylbenzoic acid, m. 69°. Under similar conditions Me thymate gave 60-70% of 2-methyl-4-methoxy-5-isopropyl-α-chlorotolnene, b16 148°, d416 1.067, nD16 1.539, converted through the ester to 2-methyl-4-methoxy-5-isopropylbenzyl alc., b18 165°, d418 1.041, nD18 1.534, crystallizing on standing for 2 months to long prisms, m. 35° (phenylurethan, m. 101°), oxidized by KMnO4 to 2-methyl-4-methoxy-5-isopropylbenzoic acid, m. 139°. Distillation of the crude alc. preparation yielded also 2,2'-dimethyl-4,4'-dimethoxy-5,5'-diisopropyldiphenylmethane, m. 73°, oxidized by Na2Cr2O7 in AcOH into colorless needles of the corresponding benzophenone, m. 139°. A mixture of 300 g. of o-nitroanisole, 220 g. of 40% HCHO and 165 g. ZnCl2 was satd. with HCl for 1.5 hrs. with agitation. The temp. rose to 80° in 15 min. and remained between 80° and 90° during the reaction. Recrystn. of the solid product gave 375 g. of the chloride, m. 85.5-6.0°. A 90% yield (170 g.) of the acetate, m. 37°, was obtained from 160 g. of the chloride by heating for 2 hrs. at 100° with 190 g. NaOAc in 400 g. AcOH. Sapon. by agitation with concd. KOH for 24 hrs. and recrystn. of the solid product from alc. produced 92% of 3-nitro-4-methoxybenzyl alc., m. 69° (phenylurethan, m. 129°), converted by cold dil. KMnO4 to 3-nitro-4-methoxybenzoic acid, m. 189.5°.

ACCESSION NUMBER: 1937:61806 CAPLUS
DOCUMENT NUMBER: 31:61806
ORIGINAL REFERENCE NO.: 31:8520g-i,8521a-g
TITLE: Synthesis of methoxybenzyl alcohols
AUTHOR(S): Quelet, Raymond; Allard, Jean; Ducasse, Joseph; Germain, Yvette
SOURCE: Bull. soc. chim. [5] (1937), 4, 1092-1101
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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GI For diagram(s), see printed CA Issue.
AB Schafer and Tollens obtained from NH4Cl, HCHO and PhCOMe a base (I) to which they ascribed the structure (PhCOCH2CH2)3N (II). The reaction is more complicated, however; in addition to I there is formed an isomer (III), which is unstable and changes into I when boiled in alc.; a rearrangement of I into III could not be effected. It is not a question of dimorphism; I and III give the same methiodide, to be sure, but their salts (HCl, picrate, chloroplatinate, chloroaurate) are different and cautious treatment with Ac2O gives different Ac derivs. M. and A. suggest, with some reserve, that the stable I has the cyclic structure CH2.CH(COPh).C(OH)Ph.CH2.CH2.NCH2CH2COPh (IV) and that it is III which has the structure II. Attempts to determine the form of union of the O atoms in I and III by oxime or semicarbazone formation gave no utilizable results; there were formed mixts. which could hardly be separated Attempts were then made to show the presence of OH groups. PhNCO reacts with neither I nor III; BzCl converts III into I, which cannot be benzoylated (at higher temps. BzCl decomposes I with formation of Bz3N). On short and cautious heating with Ac2O I and III give different Ac derivs. (V and VI), while on more energetic acetylation both give the same Ac derivative (of the labile III). The 2 Ac derivs. are insol. in acids, hence the Ac group has combined with the N atom with elimination of PhCOCH:CH2. Here it is the acyclic form, (PhCOCH2CH2)2NAc (VI), which is the stable isomer; its structure is proved by the formation of a dioximne and a disemicarbazone. PhNCO does not react with V, but SOCl2, which does not attack VI, replaces the HO group in V by Cl, giving a compound (VII) which readily splits off HCl with alc. KOH, forming an unsatd. base (VIII) in which the position of the double bond is as yet uncertain. VIII takes up 1 mol. H2 on catalytic hydrogenation, yielding a product which is apparently not homogeneous; the greater part can easily be isolated in crystalline form (IX) while the noncryst. residue is possibly a stereoisomer, since in the hydrogenation 2 C atoms become asym. S. and T. had already observed that I.HCl splits off PhCOCH:CH2 when distilled with steam. III.HCl behaves in the same way. The distillation residues give in good yield the HCl salt of a secondary base, (PhCOCH2CH2)2NH (X), stable only in the form of its salts; the free X soon disproportionates into NH3 and I. The tendency to form I is so great that X adds PhCOCH:CH2 even at 15-20°. The secondary nature of X is shown by the formation of stable N-Ac and N-Bz derivs., a nitrosamine and a urea derivative; the Ac derivative is identical with VI. Its HCl salt on distillation with steam (best superheated) in dilute solution likewise slowly splits of PhCOCH:CH2, forming the HCl salt of a primary base, PhCOCH2CH2NH2 (XI) (separated from the unchanged X.HCl only with some difficulty); the free XI, too, disproportionates into NH3 and I. Tris(β-benzoylethyl) -amine (III), m. 67°; HCl salt, m. 145°; picrate, m. 140-2°; chloroplatinate; chloroaurate, yellow, m. 168°; methiodide, m. 147-8°. 4-Hydroxy-4-phenyl-5-benzoyl-1-(β-benzoylethyl)piperidine (I), m. 150°; HCl salt, m. 199-200°; chloroplatinate, m. 207-8°; picrate, yellow, m. 154°; methiodide, identical with that of III. VI, m. 110°; dioxime, m. 210°; disemicarbazone, m. 210-12°; bis(p-nitrophenylhydrazone), m. 207-8°. V, from I heated 2-3 min. with Ac2O on the water bath, m. 160°. VII, m. 165°. 1-Acetyl-4-phenyl-5-benzoyltetrahydropyridine (VIII), m. 143°; the piperidine (IX), m. 168°. Bis(β-benzoylethyl)amine-HCl, m. 175°; chloroplatinate, m. 194-5°; chloroaurate, m. 120°; N-Bz deriv., m. 105-6°; nitrosamine, m. 114-15° (decompn.); urea, m. 187° (decompn.). β-Benzoylethylamine-HCl, m. 125°; chloroplatinate, m. 227-8° (decompn.); picrate, m. 160°.

ACCESSION NUMBER: 1935:19787 CAPLUS
DOCUMENT NUMBER: 29:19787
ORIGINAL REFERENCE NO.: 29:2535i,2536a-i
TITLE: The bases formed from acetophenone, formaldehyde and ammonium chloride
AUTHOR(S): Mannich, C.; Abdullah, S. M.
SOURCE: Ber. (1935), 68B, 113-20
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 62 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB This new synthesis consists in condensing aldehydes with HCHO and the salts of secondary amines (Me2NH, Et2NH, piperidine): Me2NH + HCHO + Me2CHCHO = H2O + Me2NCH2CMe2CHO (I). Hexahydrobenzaldehyde, because of its sensitivity, must be used in the form of its NaHSO3 compound and an extra mol. of HCHO must be employed to combine with the NaHSO3. With aldehydes having a CH2 adjacent to the CHO group, the reaction may be more complicated and result in the formation of diamino or aminohydroxy aldehydes in addition to the amino aldehydes. Thus, iso-BuCHO with 1 mol. HCHO and amine each yields chiefly the amino aldehyde (II), but with 2 mols. HCHO is formed the compound Me2CHC(CH2OH)(CH2NR2)CHO (III) which loses 1 mol. HCHO with great ease (treatment with NaHSO3 in water suffices) to form II. EtCHO with 1 mol. each of HCHO and Me2NH gives a mixture of MeCH(CH2NR2)CHO (IV) and MeC(CH2NR2)2CHO (V) but with 2 mols. each of HCHO and amine forms only V; the yields, however, are poor, and a considerable quantity of the R2NH.HCl remains unchanged. AcH, HCHO and Me2NH.HCl react at room temperature with evolution of heat but it is very difficult to isolate homogeneous products. In 1 experiment only, with 3 mols. each of HCHO and Me2NH.HCl, was there obtained a crystalline product (VI) which is so unstable in solution that it could not be recrystd. Analysis points to the composition C9H24O3N2Cl2 and its structure is probably (HCl.R2NCH2)2C(CH2OH)CHO.H2O. On hydrolysis in water in the presence of dimethylhydroresorcinol (methone, dimedone) it splits off 1 mol. HCHO at room temperature and all 3 at the b. p., while Na-Hg in faintly acid solution gives the alc. (R2NCH2)2CHCH2OH (VII). These amino aldehydes can be used for the preparation of the corresponding acids through the oxime and nitrile, and of the alc. bases, whose benzoates and p-aminobenzoates are of interest as possible anesthetics (cf. Dietrichs, C. A. 26, 1339). α,α-Dimethyl-β-dimethylaminopropionaldehyde (I), from iso-PrCHO, Me2NH.HCl and paraldehyde refluxed in absolute alc., b. 142-4°; HCl salt, hygroscopic, m. 152-3°; chlorosaurate, m. 106°; oxime, m. 57° (HCl salt, m. 163°); semicarbazone, m. 160°; p-nitrophenylhydrazone-HCl, m. 174°; methiodide, m. 219-20°; cyanohydrin, oil which cannot be distilled without decomposition α,α-Dimethyl-β-dimethylaminopropyl alc., from I in AcOH with Na-Hg, b. 166-8°; HCl salt, m. 136°; methiodide, m. 222°; benzoate-HCl, m. 153°; p-nitrobenzoate, yellow, m. 35°; p-aminobenzoate, m. 79-80°. α,α-Dimethyl-β-dimethylaminopropionitrile, from the oxime of I and boiling Ac2O, b12 172° (HCl salt, m. 145°); HCl salt of acid, m. 150-1°. α-Hydroxymethyl-α-N-piperidinomethylisovaleraldehyde (III), obtained in 70% yield as the HCl salt, m. around 145° (decomposition). α-(Dimethylaminomethyl)buytyraldehyde (11.7 g. from 21 g. PrCHO), b19 60°; HCl salt, m. 105°. α-(Dimethylaminomethyl)propionaldehyde (IV), b15 45°. α,α-Bis(dimethylaminomethyl)propionaldehyde (V), b15 83°. β-Hydroxy-α,α-bis(dimethylaminomethyl)propionaldehyde-2HCl (VI), needles with 1 H2O, m. around 105°. α-(Dimethylaminomethyl)-β-dimethylaminopropanol (VII), b11 95-102°; benzoate-HCl, m. 242°; p-nitrobenzoate-HCl, m. 223°; p-aminobenzoate-HCl, m. 230°. α,α-Dimethyl-β-diethylaminopropionaldehyde, b. 175-7° (semicarbazone, m. 124-5°); propyl alc., b12 90-1° (benzoate-HCl, m. 131-2°; p-nitrobenzoate-HCl, m. 160°; p-aminobenzoate-HCl (larocaine), m. 196°). α,α-Dimethyl-β-piperidinopropionaldehyde, b12 95° (HCl salt, m. 164°; chlorosaurate, m. 116°; chlorplatinate, m. 167°; oxime-HCl, m. 169°; semicarbazone, m. 175°; cyanohydrin; methiodide, m. 211°); propyl alc., b39 140° (HCl salt, m. 204°; benzoate-HCl, m. 152°; p-nitrobenzoate-HCl, m. 162-3°; p-aminobenzoate-HCl, m. 218°). α-(Piperidinomethyl)hexahydrobenzaldehyde, b15 140-2° (HCl salt, m. 165° (decompn.); nitrate, m. 164°; oxime-HCl, m. 178°; methiodide, m. 160°); benzyl alc., b15 155-7° (HCl salt, m. 181°; methiodide, m. 148°; benzoate-HCl, m. 177°; p-nitrobenzoate-HCl, m. 134°; p-aminobenzoate-HCl, m. 230°). α-(Dimethylaminomethyl)hexahydrobenzaldehyde, b17 102-4° (HCl salt, m. 130°; oxime-HCl, m. 179°; methiodide, m. 223°); benzyl alc., b20 127-9° (HCl salt, m. 144°; methiodide, m. 178°; benzoate-HCl, m. 145°; p-nitrobenzoate-HCl, m. 185°; p-aminobenzoate-HCl, m. 193°). α-(N-Piperidinomethyl)isovaleraldehyde, b18 119-20° (HCl salt, m. 142° (decompn.)); isoamyl alc., b17 134-6° (benzoate-HCl, m. 155°; p-nitrobenzoate-HCl, m. 189°; p-aminobenzoate-HCl, m. 222°). α-Hydroxymethyl-α-(dimethylaminomethyl)isovaleraldehyde, m. 149° (decompn.). α-(Dimethylaminomethyl)isovaleraldehyde, b13 63-6° (HCl salt, m. 120° (decompn.); methiodide, m. 145°; oxime-HCl, m. 133°); isoamyl alc., b13 80° (benzoate-HCl, m. 180°; p-nitrobenzoate-HCl, m. 176°; p-aminobenzoate-HCl, m. 167°). α-(Dimethylaminomethyl)butanol, b14 70-1° (HCl salt, m. 81°; benzoate-HCl, m. 159°; p-nitrobenzoate-HCl, m. 163°; p-aminobenzoate-HCl, m. 163°). α-(Dimethylaminomethyl)propanol, b12 60-5° (benzoate-HCl, m. 142°; p-nitrobenzoate-HCl, m. 183°; p-aminobenzoate-HCl, m. 165°). α,α-Bis(dimethylaminomethyl)propanol, b12 100-2° (benzoate-HCl, m. 196°; p-vitrobenzoate-HCl, m. 209°).

ACCESSION NUMBER: 1932:28310 CAPLUS
DOCUMENT NUMBER: 26:28310
ORIGINAL REFERENCE NO.: 26:2965g-i,2966a-g
TITLE: A synthesis of N-substituted α-amino aldehydes
AUTHOR(S): Mannich, C.; Lesser, B.; Silten, F.
SOURCE: Ber. (1932), 65B, 378-85
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 63 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB cf. C. A. 16, 2497. In view of the importance of plant syntheses, it is interesting to find that simple amine salts give, with CH2O, complicated N compds. under comparatively mild conditions. M. and L. have studied the reaction between sec. amines, CH2O and aliphatic-aromatic ketones. The reaction is as follows: MeOC6H4COMe + CH2O + HNC5H10.HCl = H2O + MeOC6H4COCH2CH2NC5H10.HCl. The reaction in most cases proceeds easily and with good yields. It is carried out by boiling a mixture of the HCl salt of the amine with concentrated CH2O solution and the ketone for 1 hr.; better still by warming the amine salt and the ketone with paraformaldehyde in alc. A large number of β-keto bases can be thus prepared, inasmuch as both the amine and the ketone may be varied widely. In exceptional cases the reaction does not proceed normally. The keto bases so obtained in the form of their solid HCl salts are relatively stable. Aqueous solns. on boiling decompose to give the amine and an unsatd. ketone. Superheated steam or dry distillation in vacuo produces the same effect. E. g., p-MeOC6H4COCH2CH2NMe2 gives NHMe2.HCl and MeOC6H4COCH2:CH2, the latter in poor yield due to polymerization. The vinyl compound on reduction, yields propionanisone. Some of the free keto bases are solid; the liquid ones cannot be distilled in vacuo. The keto bases give normal oximes except in case of the NMe2 derivs. The keto groups may be reduced by various well known methods. This synthesis of β-keto bases makes possible the synthesis of compds. of the type of adrenaline, tyramine, hordenine, etc., but with the N in the γ-position. The corresponding homolog of adrenaline caused no rise of blood pressure, but a fall. However, the C6H6 derivs. of the type PhCOCH2CH2NC5H10 are local anesthetics. Replacement of the Ph group by other groups also gave anesthetic compds. Reduction of the keto bases to the β-NH2 alcs. caused loss of anesthetic properties, but benzoylation caused marked anesthesia. The Bz group and the N are here in the same positions as in cocaine. Some of these compds. produced are more anesthetic than cocaine, but are irritating. The p-H2NC6H4CO2H esters of these 1,3-amino alcs. are anesthetics. β-Piperidinoethyl phenyl ketone hydrochloride, obtained by boiling in absolute alc. C5H11N.HCl, paraformaldehyde and PhCOMe, leaflets from EtOH-Me2CO, m. 192-3°, readily soluble in H2O, MeOH, CHCl3, difficultly in alc., Me2CO, and EtOAc. Boiling in aqueous solution causes decomposition with formation of CH2:CH2COPh. The free base is a nondistillable oil. Picrate, needles from HOAc, m. 180.5°. Oxime, needles from dilute alc., m. 143°. 1,6-Dipiperidino-3,4-diphenylhexane-3,4-diol (α- and β-forms), prepared by placing a moist Et2O solution of the above ketone in contact with activated Al and extracting with Et2O in a Soxhlet, needles from CHCl3, m. 238° with brown coloration. HCl salt, m. 270°. This is the α-form. The β-form, obtained from the mother liquors of the α-form by treatment with HCl, followed by alkali, plates from alc., m. 115°. Probably one of these forms is the dl-, the other the meso-compound [β-Piperidinoethyl]phenylcarbinol, by reduction of the HCl salt of the corresponding ketone base in H2O by H and palladiumized charcoal; HCl salt, crystals from CHCl3-EtOAc, m. 138°. Treatment with NH4OH gives an oil crystallizing from MeOH, in leaflets, m. 68-9°. Picrate, needles, m. 103°. The same is obtained by reduction with Zn dust and HI. Hydrochloride of benzoate, by the action of BzCl on the base in CHCl3, flat needles, m. 170°, is strongly anesthetic. p-Nitrobenzoyl ester, by boiling the base in C6H6 with p-O2NC6H4COCl, brown needles from alc., m. 104°. p-Aminobenzoate, from the NO2 compound with Sn and HCl at 40°, needles from ether, m. 118°; solns. of the HCl salt are strongly anesthetic. β-Tetrahydroisoquinolinoethyl phenyl ketone hydrochloride, by boiling tetrahydroisoquinoline-HCl in abs. alc. with paraformaldehyde and PhCOMe, m. 188°. The free base is a viscous oil, crystg. in an ice mixt. N,N'-Bis-[β-benzoylethyl]piperazine, prepd. in a similar manner from piperazine; the HCl salt turns brown at 190° without melting; the free base, by treatment with NH3, crystals from 70% alc., m. 141°. Picrate, needles from PhNO2, decomps. above 190°. Dioxime, m. 245°. β-Dimethylaminoethyl p-methoxyphenyl ketone, prepd. from acetoanisone, paraformaldehyde, and Me2NH.HCl, crysts. as the HCl salt, needles from alc. m. 181°. Picrate, needles, m. 145°.

By heating the HCl salt under 20 mm. at 180°, it decomps. to Me2NH.HCl and vinyl anisyl ketone, m. 19°, unstable in liquid form, undergoing polymerization; dibromide, by the action of Br in CHCl3, prisms from ligroin, m. 71°. Alc. PhNHNH2 boiled with the ketone gives crystals, m. 105°, probably of 1-phenyl-3-p-methoxyphenylpyrazoline. Et anisyl ketone, prepd. by reduction of the vinyl ketone, is identical with Klages' product (Ber. 35, 2262(1902)). β-Dimethylaminoethyl p-hydroxyphenyl ketone, prepd. from the corresponding MeO compd. by boiling with HI. Hydroiodide, light yellow leaflets from alc., m. 205°. Alkalies do not cause sepn. of the free base from its aq. solns. [β-Dimethylaminoethyl]-p-anisylcarbinol hydrochloride, by reduction of the keto base with H and Pd, needles from CHCl3-EtOAc, m. 203-4°. Free base, b30 146-8°, m. 53°. Benzoate, from the carbinol and BzCl in CHCl3; on addn. of EtOAc, the HCl salt, m. 174°, seps. It is a powerful anesthetic. β-Piperidino-ethyl p-anisyl ketone, from C5H11N.HCl, acetoanisone, and paraformaldehyde; HCl salt, needles, m. 216°. The free base is an oil which solidifies in an ice mixt. Picrate, short needles, m. 165°. Oxime, needles from alc., m. 136°. N,N'-Bis-[β-p-anisoyl-ethyl]piperazine, from piperazine, HCl, acetoanisone, and paraformaldehyde. The HCl salt becomes brown at 150° without melting. Free base, yellowish leaflets, m. 173°, turning brown at 171°. β-Piperidinoisopropyl p-anisyl ketone, prepd. in a similar manner from Et p-anisyl ketone; HCl salt, leaflets from abs. EtOH-Me2CO, m. 178°. The free base is an oil. Oxime, m. 94°. β-Dimethylaminoethyl 3,4-dimethoxyphenyl ketone, by heating acetoveratrone, Me2NH.HCl, and paraformaldehyde in abs. alc., is a viscous oil. The HCl salt m. 181-2°; picrate, needles, m. 157°. β-Dimethylaminoethyl 3,4-dihydroxyphenyl ketone hydroiodide, from the above MeO compd. with HI, light yellow crystals, m. 196°. Alkalies give no ppt. I+[γ-Dimelhylaminopropyl]-3,4-dimethoxybenzene hydrochloride, by reduction of the HCl salt of the corresponding keto base by H and Pd, needles from Me2CO, m. 195°. Free base, colorless and odorless oil, b30 161-4°. β-Piperidinoethyl 3,4-dimethoxyphenyl ketone, prepd. from C5H11N.HCl, acetoveratrone, and paraformaldehyde; HCl salt, prisms, m. 183°. Free base, m. 113°. Picrate, m. 180°. Oxime, needles from alc., m. 168°. N,N'-Bis-[β-veratroylethyl]-piperazine, prepd. in a similar manner from piperazine; HCl salt, short needles from 10% HCl, decomp. at 150° with brown coloration. Free base, yellow needles, m. 168°. β-Diethylaminoethyl veratryl ketone hydrochloride, prepd. from Et2NH.HCl by the usual method, needles from EtOAc, m. 140-1°. The free base is a nondistillable oil. Picrate, m. 136°; oxime, m. 104°. 1-Piperidino-2,3-diphenyl-3-propanone, prepd. from desoxybenzoin, C5H11NH.HCl, and paraformaldehyde, crystals from 90% alc., m. 91°. The HCl salt is hygroscopic, but the HNO3 salt forms difficultly sol. needles, m. 117°. β-[α-Dimethylaminopropio]tetralin, prepd. from acetotetralin; HCl salt, needles from Me2CO, m. 170°. The free base is an oil;

L19 ANSWER 63 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
picrate, needles, m. 156°. D-Dimethylaminoethyl-β-ar-tetrahydronaphthylcarbinol, prepd. by reducing the HCl salt of the above keto base with H and Pd; HCl salt, leaflets from Me2CO, m. 163°. The free base is an oil. β-[o-Piperidinopropio]-tetralin; HCl salt, needles from Me2CO, m. 170°, crysts. from water with water of crystn. and m. 85°. This free base is an oil. Nitrate, difficultly sol. in water, m. 134-5°. Oxime HCl salt, silky needles from dil. alc., m. 211°.

ACCESSION NUMBER: 1923:10265 CAPLUS
DOCUMENT NUMBER: 17:10265
ORIGINAL REFERENCE NO.: 17:1795b-i,1796a-i,1797a-b
TITLE: Synthesis of β-keto bases from aliphatic-aromatic ketones, formaldehyde, and secondary amines
AUTHOR(S): Mannich, C.; Lammring, D.
SOURCE: Ber. (1922), 55B, 3510-26
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 17:10265

L19 ANSWER 64 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB Chemical reactions in solid, liquid, and gaseous substances, which are liable to disturbance by exothermic heating, are effected by heating the finely divided substance or mixture of substances by passage through molten metal kept at a suitable temperature; by the rapid distribution of any locally developed heat to the molten metal, undesired secondary reactions are avoided. Examples of reactions to which the invention may be applied are the destructive distillation of wood, the oxidation of CH4 to HCHO, and, according to the provisional specification, the distillation of Ca acetate; thus, finely subdivided wood such as sawdust or shavings is fed to a bath of molten lead at 350° and caused to travel therethrough by a rotating drum or by means of a travelling endless band, as described in 174,974; a mixture of CH4 and air or O is passed in the form of fine bubbles through molten metal heated to 350-400°, preferably in the still described in 170,617, (C. A. 16, 1119) the mixed gases being pumped into the hood and issuing therefrom as fine bubbles into the corrugations of the inclined plate.

ACCESSION NUMBER: 1922:13648 CAPLUS
DOCUMENT NUMBER: 16:13648
ORIGINAL REFERENCE NO.: 16:2376d-g
TITLE: Effecting chemical reactions
PATENT ASSIGNEE(S): Thermal Industrial & Chemical (T.I.C.) Research Co., Ltd.; Morgan, J. S.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 176438		19201102	GB	

L19 ANSWER 65 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
AB In the early days of the natural gas industry, there were frequent cases of trouble in the mains caused by condensation of certain hydrocarbons. This was eliminated by the installation of drips from which the condensate, called "drip gasoline," was periodically removed and refined. About this time Mr. George Seybolt conceived the idea that there might be enough of these heavier hydrocarbons to pay for extn., and designed an apparatus which has proved very successful for this purpose. Natural gas is composed almost entirely of paraffin hydrocarbons, the lighter ones of the series being practically fixed, but the heavier being condensed with moderately low temps. and increased pressures. This condensate, consisting largely of pentane and hexane, forms an exceptionally high-test motor fuel and may be mixed with low-test gasoline to form a much larger quantity of a quality which is still acceptable. Moreover, aside from motor fuel, there are many valuable uses for these products. A fraction distilling between 40 and 70°, and consisting essentially of pentane and hexane, is chlorinated in the presence of ultraviolet light, amyl chloride distilled from the mixture, and the product heated under pressure with sodium acetate to form amyl acetate and salt, the former being a valuable solvent. A great potential possibility lies in the production of fatty acids for foods from hexane, heptane and octane; further, by simple "cracking" operations benzene and toluene can be produced. Other products are propane and butane; they remain in the by-product vapors from the condenser after passing under pressure through an absorbent oil, and are condensed and separated by certain conditions of temperature and pressure. These gases, compressed in cylinders, are used for lighting isolated buildings and as fuel for stationary and automobile engines, a mixer being used in place of a carburetor. Tables show the power of performance to be much better than with gasoline. As a torch fuel for metal cutting and welding, butane has the advantages of a narrow explosive range and low liquifying pressure. Researches on the behavior of natural gas, vent tank gas, propane and butane, when subjected to heat in the presence of catalysts have shown that the products resulting were characteristic for each catalyst or each set of conditions. An industrial application occurs in the production of carbon black which, after yielding the product desired, gives a volume of gas 1.27 to 2.99 times larger than the original and still has a heating value much superior to that of any artificial gas. However, this discharge gas contains unsatd. hydrocarbons of the olefin series which may be removed and used if desired to produce glycols, industrial alcohol, acetaldehyde, acetic acid, acetone, chlorinated olefine solvents, and other derivatives. Under the heading "Reactions with Air or Oxygen" the author takes up a number of patents on the production of methyl alcohol, formaldehyde, formic acid, carbon dioxide, and secondary products such as phosgene and oxalic acid; and under "Reactions with Chlorine" he discusses carbon tetrachloride, chloroform, methylene chloride, and muriatic acid. He shows also how the exhaust gas of a gas engine can be separated by means of compression and absorption into H2O, CO2, N, and argon, which, in turn, are utilized in various chemical industries. Also in Gas Age 41, 555-60(1918).

ACCESSION NUMBER: 1918:10678 CAPLUS
DOCUMENT NUMBER: 12:10678
ORIGINAL REFERENCE NO.: 12:1826c-i,1827a-b
TITLE: Whole natural gas industry today responsive to problem of chemical possibilities of natural gas
AUTHOR(S): Garner, J. B.
SOURCE: American Gas Engineering Journal (1918), 108, 489-95,505-8
CODEN: AGEJAN; ISSN: 0096-4387

L19 ANSWER 65 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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     FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005
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L2         61794 S 50-00-0/RN
L3        166261 S N-METHYL?
L4       1415128 S ?AMINE
L5           889 S L2 AND L3 AND L4
L6        362618 S DISTILL?
L7            47 S L5 AND L6
L8        135208 S FORMALDEHYDE
L9         53548 S L8 AND L2
L10       143454 S L8 OR L2
L11         3718 S L10 AND L3
L12         2315 S L11 AND L4
L13         2268 S L12 NOT L7
L14           36 S L13 AND L6
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=> s paraformaldehyde/cn
L20             1 PARAFORMALDEHYDE/CN

=> d l20
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L20 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2005 ACS on STN
RN 30525-89-4 REGISTRY
ED Entered STN: 16 Nov 1984
CN Paraformaldehyde (9CI) (CA INDEX NAME)
OTHER NAMES:
CN Aldacide
CN Flo-Mor
CN Paraform
DR 53026-80-5
MF (C H2 O)x
CI PMS, COM
PCT Polyether, Polyether formed
LC STN Files: ADISNEWS, AGRICOLA, ANABSTR, AQUIRE, BIOBUSINESS, BIOSIS, BIOTECHNO, CA, CABA, CANCERLIT, CAPLUS, CASREACT, CBNB, CEN, CHEMCATS, CHEMLIST, CHEMSAFE, CIN, CSCHEM, CSNB, DDFU, DETHERM*, DIOGENES, DRUGU, EMBASE, HSDB*, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MRCK*, MSDS-OHS, NIOSHTIC, PDLCOM*, PIRA, PROMT, PS, RTECS*, SPECINFO, TOXCENTER, ULIDAT, USAN, USPAT2, USPATFULL, VETU, VTB
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L1             1 S FORMALDEHYDE/CN

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L6        362618 S DISTILL?
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L15       411299 S SECONDARY
L16         1271 S L15 AND L9
L17           72 S L16 AND L6
L18           65 S L17 NOT L7
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L19          65 S L18 NOT L14

     FILE 'REGISTRY' ENTERED AT 17:18:49 ON 15 JUN 2005
L20           1 S PARAFORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 17:19:34 ON 15 JUN 2005

=> s paraformaldehyde/cn
   REG1stRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.



L22        5424 L21

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COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
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FULL ESTIMATED COST                                       0.45     451.50

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FILE LAST UPDATED: 14 Jun 2005  (20050614/ED)

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  substance identification.

=> s paraformaldehyde/cn
   REG1stRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
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L24       5424 L23

=> s 30525-89-4/rn
          5424 30525-89-4
           452 30525-89-4D
L25       5027 30525-89-4/RN
                (30525-89-4 (NOTL) 30525-89-4D )

=> s l24 or l25
L26       5424 L24 OR L25

=> d his

     (FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005)

     FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005
L1             1 S FORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005
L2         61794 S 50-00-0/RN
L3        166261 S N-METHYL?
L4       1415128 S ?AMINE
L5           889 S L2 AND L3 AND L4
L6        362618 S DISTILL?
L7            47 S L5 AND L6
L8        135208 S FORMALDEHYDE
L9         53548 S L8 AND L2
L10       143454 S L8 OR L2
L11         3718 S L10 AND L3
L12         2315 S L11 AND L4
L13         2268 S L12 NOT L7
L14           36 S L13 AND L6
L15       411299 S SECONDARY
L16         1271 S L15 AND L9
L17           72 S L16 AND L6
L18           65 S L17 NOT L7
L19           65 S L18 NOT L14

     FILE 'REGISTRY' ENTERED AT 17:18:49 ON 15 JUN 2005
L20            1 S PARAFORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 17:19:34 ON 15 JUN 2005
                S PARAFORMALDEHYDE/CN

     FILE 'REGISTRY' ENTERED AT 17:19:47 ON 15 JUN 2005
L21            1 S PARAFORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 17:19:47 ON 15 JUN 2005
L22         5424 S L21

     FILE 'CAPLUS' ENTERED AT 17:19:54 ON 15 JUN 2005
                S PARAFORMALDEHYDE/CN

     FILE 'REGISTRY' ENTERED AT 17:20:06 ON 15 JUN 2005
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L23             1 S PARAFORMALDEHYDE/CN

     FILE 'CAPLUS' ENTERED AT 17:20:07 ON 15 JUN 2005
L24          5424 S L23
L25          5027 S 30525-89-4/RN
L26          5424 S L24 OR L25

=> s l26 and l3
L27           344 L26 AND L3

=> s l27 and l4
L28           212 L27 AND L4

=> s l28 and l6
L29             9 L28 AND L6

=> d l29 1-9 abs ibib
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L29 ANSWER 1 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB In a process for production of an aromatic azomethine by reaction of an aniline with formaldehyde, formaldehyde is provided in the form of a product produced by contacting paraformaldehyde with from about 0.25 to about 3 mol equivalent of an aliphatic alc. having from 1 to 4 carbon atoms in the presence of a catalytic amount of a base. The azomethine may then be used to produce a haloacetanilide. Thus, e.g., one reactor was charged with 3.0 mol paraformaldehyde, 3.0 mol ethanol, 0.01 mol triethylamine, 1.0 mol xylene and 0.5 mol water, heated to 85-90° and agitated until the solution was clear; this solution was added to a reactor containing 1 mol of 2-methyl-6-ethylaniline and 2 mol of xylene at about 90°; the reaction was allowed to proceed with azeotropic distillation of water at atmospheric pressure at 95-126°; addition of chloroacetyl chloride afforded 96-97% of the N-chloromethyl-α-chloroacetanilide derivative

ACCESSION NUMBER: 1995:603984 CAPLUS
DOCUMENT NUMBER: 123:111656
TITLE: Process for producing aromatic azomethines by reaction of an aniline with formaldehyde provided in the form of a formaldehyde-alcohol complex
INVENTOR(S): Rodriguez, Gilbert
PATENT ASSIGNEE(S): Imperial Chemical Industries PLC, UK
SOURCE: U.S., 7 pp. Cont.-in-part of U.S. Ser. No. 680,468, abandoned.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5399759	A	19950321	US 1992-872775	19920422
HU 65592	A2	19940728	HU 1993-2620	19920320
HU 219568	B	20010528		
AT 154000	E	19970615	AT 1992-910655	19920320
ES 2102503	T3	19970801	ES 1992-910655	19920320
ZA 9202455	A	19930329	ZA 1992-2455	19920403
IL 101484	A1	19970415	IL 1992-101484	19920403
PRIORITY APPLN. INFO.:			US 1991-680468 B2	19910404

OTHER SOURCE(S): CASREACT 123:111656; MARPAT 123:111656

L29 ANSWER 2 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB The hazardous materials regulations under the Federal Hazardous Materials Transportation Act are revised based on the United Nations recommendations on the transport of dangerous goods. The regulations cover the classification of materials, packaging requirements, and package marking, labeling, and shipping documentation, as well as transportation modes and handling, and incident reporting. Performance-oriented stds. are adopted for packaging for bulk and nonbulk transportation, and SI units of measurement generally replace US customary units. Hazardous material descriptions and proper shipping names are tabulated together with hazard class, identification nos., packing group, label required, special provisions, packaging authorizations, quantity limitations, and vessel stowage requirements.

ACCESSION NUMBER: 1992:135528 CAPLUS
DOCUMENT NUMBER: 116:135528
TITLE: Performance-oriented packaging standards; changes to classification, hazard communication, packaging and handling requirements based on UN standards and agency initiative
CORPORATE SOURCE: United States Dept. of Transportation, Washington, DC, 20590-0001, USA
SOURCE: Federal Register (1990), 55(246), 52402-729, 21 Dec 1990
CODEN: FEREAC; ISSN: 0097-6326
DOCUMENT TYPE: Journal
LANGUAGE: English

L29 ANSWER 3 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

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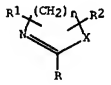

I

AB Oxazoline and imidazoline derivs. [I; R = C1-19 hydrocarbon, alkoxyalkyl, haloalkyl, trifluoromethyl, alkoxy, amino, alkylamino; R1, R2 = H, alkyl, trifluoromethyl, alkoxyalkyl, aminoalkyl, alkyl, and acrylaminoalkyl, etc.; X = O, NR3 (R3 = H, alkyl, alkenyl, alkoxyalkyl, carbalkoxyalkyl etc.) n = 2-3] are prepared as penetration enhancers. 2-(2-Aminoethylamino)ethanol and Et dodecanoate were heated before Et was replaced with toluene and refluxed to remove water than distilled to give 1-(2-hydroxyethyl)-2-undecyl-2-imidazoline (II). A cream formulation containing isosorbide dinitrate 0.7 and II 2% was applied on the human stratum corneum and then it was put between diffusion cells. The average cumulative amount of II in the receptor side of diffusion cell after 48 h was 872 μg as compared to 535 for control with no II. Several topical formulation of therapeutic agents with above penetration enhancers are given.

ACCESSION NUMBER: 1991:663486 CAPLUS
DOCUMENT NUMBER: 115:263486
TITLE: Preparation of onazoline and imidazoline derivatives as body-membrane penetration enhancers
INVENTOR(S): Rajadhyaksha, Vithal J.
PATENT ASSIGNEE(S): USA
SOURCE: U.S., 17 pp. Cont.-in-part of U.S. 4,876,249.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5030629	A	19910709	US 1989-393584	19890811
US 4876249	A	19891024	US 1987-2387	19870112
PRIORITY APPLN. INFO.:			US 1987-2387 A2	19870112
			US 1989-345457 B2	19890501

OTHER SOURCE(S): MARPAT 115:263486

L29 ANSWER 4 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB RNHCH2P(O)(OH)2 (I; R = alkyl, aralkyl cycloalkyl), useful as dye intermediates, herbicides (no data), and fire retardants on cellulosic materials, were prepared MeNHAc, AcOH, Ac2O, and paraformaldehyde were heated at 116° for 30 min and the mixture was cooled to 25. PCl3 was added, and the mixture was kept at 59-70° for 45 min followed by heating to 130° over 3 h. The mixture was cooled to 100° and H2O was added, followed by distillation of H2O/HOAc. Aqueous H2SO4 was added and the mixture was refluxed 6 h. MeOH was added to precipitate I (R = Me).

ACCESSION NUMBER: 1989:595080 CAPLUS
DOCUMENT NUMBER: 111:195080
TITLE: Process for preparation of substituted-aminomethylphosphonic acids as herbicides, fire retardants, and dye intermediates
INVENTOR(S): Feeman, James F.
PATENT ASSIGNEE(S): Crompton and Knowles Corp., USA
SOURCE: U.S., 6 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4830788	A	19890516	US 1987-123222	19871120
CA 1338739	A1	19961126	CA 1989-591143	19890215
JP 02221288	A2	19900904	JP 1989-40456	19890222
JP 05043713	B4	19930702		
EP 385014	A1	19900905	EP 1989-302181	19890303
R: AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, LU, NL, SE				
PRIORITY APPLN. INFO.:			US 1987-123222	19871120

OTHER SOURCE(S): CASREACT 111:195080; MARPAT 111:195080

L29 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN
AB The title compds. H2C:CR1CONHCH2OR2 (R1 = H, Me; R2 = Bu, CH2CHMe2, CHMeEt, CMe3), useful as crosslinking monomers for coatings, are manufactured by hydroxymethylating H2C:CR1CONH2 with HCHO in R2OH in the presence of an alkaline catalyst, etherifying the resulting H2C:CR1CONHCH2OH with addnl. R2OH in the presence of an acid catalyst, and distilling off the solvent at pH 2-5. Thus, 71.7 g acrylamide was treated with 56.3 g paraformaldehyde in 37.1 g BuOH at pH 10.0 (by Et3N) at 50° to give N-methylolacrylamide (I), which was treated with addnl. 425.2 g BuOH under reflux at pH 3.0 (by oxalic acid). The reaction mixture was readjusted at pH 3.0 by oxalic acid and concentrated under reduced pressure at 90° to give 163.2 g product containing N-butoxymethylacrylamide 98.2, I 0.3, and acrylamide 1.5%.

ACCESSION NUMBER: 1988:205254 CAPLUS
DOCUMENT NUMBER: 108:205254
TITLE: Method of making N-alkoxymethyl(meth)acrylamides
INVENTOR(S): Watanabe, Seiichi; Sakasai, Kazuya; Tanaka, Yoshinori
PATENT ASSIGNEE(S): Mitsui Toatsu Chemicals, Inc., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 5
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63005068	A2	19880111	JP 1986-146828	19860625
JP 07033362	B4	19950412		
PRIORITY APPLN. INFO.:			JP 1986-146828	19860625

OTHER SOURCE(S): CASREACT 108:205254; MARPAT 108:205254

L29 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN
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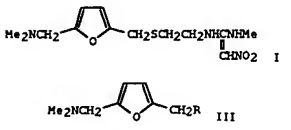

AB The title compound (I) [i.e. ranitidine] is prepared from furfuryl alc. (II) via the intermediate (dimethylaminomethyl)furanylmethyl derivs. III (R = OH) and III (R = Br). Condensation of II with paraformaldehyde and Me2NH.HCl in Me2CHOH at reflux, followed by evaporation, extraction, and distillation in vacuo, gave 62% III (R = OH). A solution of the latter in refluxing dichloroethane was treated dropwise with SOBr2 in dichloroethane, followed by 8 h reflux, evaporation, and distillation in vacuo, to give 78% III (R = Br). The bromide was added dropwise over 4-5 h to a solution of HSCH2CH2NHC(:CHNO2)NHMe and KOH in Me2CHOH at -2°, and the mixture was stirred for 20 h at room temperature, filtered, saturated with HCl(g), and set aside to precipitate crystalline I.HCl.

ACCESSION NUMBER: 1988:150297 CAPLUS
DOCUMENT NUMBER: 108:150297
TITLE: Process for the preparation of the antiulcer agent N-[2[[[5-[(dimethylamino)methyl]-2-furanyl]methyl]thio]ethyl-N'-methyl-2-nitro-1,1-ethenediamine
INVENTOR(S): Linan Castellet, Isidro
PATENT ASSIGNEE(S): Farmhispania S. A., Spain
SOURCE: Span., 7 pp.
CODEN: SPXXAD
DOCUMENT TYPE: Patent
LANGUAGE: Spanish
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ES 556593	A1	19870716	ES 1986-556593	19860625
PRIORITY APPLN. INFO.:			ES 1986-556593	19860625

L29 ANSWER 7 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN
AB The title compds., HCONR1CH2NHCOCR2:CHR3 (R1 = H or C1-5 alkyl, and R2, R3 = H or Me) are prepared for copolymn. with unsatd. olefinic monomers to give self-crosslinking thermosetting copolymers. Thus, HCONH2 450 and paraformaldehyde 300 g are stirred at 110° for 1 hr to give N-methylolformamide, cooled to 40°, and 2 l. cyclohexane, 30g. hydroquinone Me ether, 710 g acrylamide, and 75 ml concentrated HCl are added; water is azeotropically distilled to give 97% yield of N-formyl-N'-acryloylmethylenediamine. A 20:336:20 (weight) acrylonitrile-butyl acrylate-N-acryloyl-N'-formylmethylenediamine polymer is prepared at 46-50° as a 38.7% aqueous dispersion (pH 2.4). Drying the dispersion at 95° gives a crosslinked, flexible, and insol. film.

ACCESSION NUMBER: 1975:459739 CAPLUS
DOCUMENT NUMBER: 83:59739
TITLE: Methylene diamine derivatives
INVENTOR(S): Ribka, Joachim; Piesch, Steffen; Engelhardt, Friedrich
PATENT ASSIGNEE(S): Cassella Farbwerke Mainkur A.-G.
SOURCE: Ger. Offen., 17 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2251921	A1	19740425	DE 1972-2251921	19721023
NL 7314178	A	19740425	NL 1973-14178	19731015
CA 997371	A1	19760921	CA 1973-183604	19731017
DD 109616	C	19741112	DD 1973-174175	19731019
FR 2203807	A1	19740517	FR 1973-37556	19731022
JP 49075522	A2	19740720	JP 1973-118012	19731022
AU 7361640	A1	19750424	AU 1973-61640	19731022
AT 7308922	A	19750915	AT 1973-8922	19731022
AT 330142	B	19760610		
GB 1412893	A	19751105	GB 1973-49023	19731022
SU 503505	D	19760215	SU 1973-1966744	19731022
IT 998840	A	19760220	IT 1973-30409	19731022
ES 419839	A1	19760401	ES 1973-419839	19731022
CH 589612	A	19770715	CH 1973-14866	19731022
BE 806399	A1	19740423	BE 1973-136964	19731023
US 3912780	A	19751014	US 1973-408486	19731023
CS 172877	P	19770128	CS 1973-7278	19731023
PRIORITY APPLN. INFO.:			DE 1972-2251921 A	19721023

L29 ANSWER 8 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN
AB Foam-in-place polyurethans of improved temperature and moisture resistance are prepared by treating a polyisocyanate with a polyhydroxy compound, obtained by condensation of an aldehyde with a polyalc. which does not form cyclic acetals with HCHO. Thus, a mixture of 1,4-butanediol 900, (4-HOCH2CH2OC6H4)2CMe2 316, paraformaldehyde 330 g., and 800 cc. C6H6 was refluxed, 3 g. p-toluenesulfonic acid added, the C6H6-H2O azeotrope distilled, and the residual C6H6 removed by vacuum distillation to give the polyacetal (I) (OH number 65). Then, 87 g. MeC6H3(NCO)2 (II) was added dropwise with stirring to a mixture of 1 kg. I, 20 g. N-methyl-diethanolamine, and 20 g. triethanolamine at 90-100°. The mixture was heated an addnl. 0.5 hr. to give a resinous product (III) with a OH number of 54. III (200 g.), 4 g. of a mixture of oleic acid and diethylbis(hydroxyethyl)ammonium ion (not further defined), 4 g. water, and 60 g. II were mixed until foaming began to give a soft, cellular polyurethan, bulk d. 0.086 g./cc., elasticity 30%, tensile strength 1.62 kg./sq. cm., elongation 123%, resistance to further tearing 0.74 kg./cm., and compression hardness at 40% compression 156 kg./sq. cm.

ACCESSION NUMBER: 1959:20554 CAPLUS
DOCUMENT NUMBER: 53:20554
ORIGINAL REFERENCE NO.: 53:3771b-d
TITLE: High-molecular-weight polyurethan plastics
PATENT ASSIGNEE(S): Farbenfabriken Bayer Akt.-Ges.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 798209		19580716	GB	
US 2961428		1960	US	

L29 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB EtOH (90 cc.) containing 0.5 g. Na and 75 g. CF2:CF2 (I) shaken under N in a bomb 8 h. at 50° and the mixture distilled through a precision column give 101.7 g. HCF2-CF2OEt, b. 57.5°, nD25 1.294, d425 1.1978. I and (CH2OH)2 treated in the same way give 9% (HCF2CF2OCH2)2, b100 86°, nD25 1.3202, d425 1.4726, and 15% HCF2CF2OCH2-CH2OH, b100 94°, nD25 1.3418, d425 1.4159. In a similar way the following HCF2CF2OR are prepared: R = C12H25, 99% yield, b4 105°, nD25 1.3968, d425 0.9831; C18H37, 80%, b6 170°, m. 20-3°, nD25 1.4144, d425 0.9530; C6H11 99%, b100 86°, nD25 1.3848, d425 1.1526. When 100 g. Na2CO3 in 200 cc. H2O buffered with Na2HPO4 or borax to pH 6-7 is shaken 9 h. in a N atmospheric in a Ag-lined bomb with so much I that the pressure at 120° is 350 lb., with readjustment of the pressure to 350 lb. whenever it has dropped to about 325 lb., 17 g. NaF is formed. The filtrate is evaporated to dryness, the residue extracted with EtOH, and the filtered EtOH extract evaporated on a steam bath, giving 177 g. salts (II), m. 175°. II (165 g.) treated with 135 cc. 35% H2SO4, the Na2SO4 filtered off, the filtrate extracted with ether, and the residue of the dried ether extract distilled, gives 75 g. HCF2CF2SO3H.H2O (III), b5 112-14.5°, m. 54°. III is very hygroscopic. Warming 40 g. III 1 h. with 35 cc. SOCl2 under a reflux condenser and distilling the product give 100% HCF2CF2SO3H (IV), b3.5 90-2°. The following HCF2CF2SO3NH3R salts are prepared: R = H, m. 198° (Maquenne block); Me, m. 119-20.5°; C12H25, m. 155°; Ph, m. 235°, also formed when III is treated with PhNCO; 1-C10H7, m. 225°, also obtained from III and 1-C10H7NCO. Anhydrous III (81 g.) with 100 g. PCl5 gives HCF2CF2SO2Cl, b. 92-2.5°. I with NHRR' gives the following HCF2-CONRR' (R,R' given): H, Bu, 90% yield, b30 113°, nD25 1.4112, d425 1.1029; Bu, Bu, 62%, b10 107°, nD25 1.4270, d425 1.0158; H, Ph, 71%, b5 114°, m. 58°; Me, Ph, 51% b4 104°, nD25 1.5036, d425 1.2305. I (75 g.) and 50 g. NH3 in 100 cc. ether containing 0.1 g. Cu(OAc)2 under anhydrous conditions give, in an exothermic reaction, 82% 2,4,6-tris(difluoromethyl)-s-triazine (V), b9 73°, m. 24.5°, nD25 1.3999, d425 1.5973. V does not react with Br in CCl4, with dilute KMnO4, or dilute HNO2. Refluxing 22 g. V with 70 cc. 4 N NaOH 4 h., acidifying the aqueous filtrate with 30 cc. 50% H2SO4, and extracting it with ether give 22% HCF2CO2H, b. 131°. When 50 g. V is refluxed 50 h. with 75 cc. H2O 7 g. V is recovered; the aqueous solution on evaporation gives 50 g. HCF2CO2NH4. Heating 15 g. paraformaldehyde, 150 cc. concentrated H2SO4, and 50 g. I in a Ag-lined vessel 15 h. at 80°, pouring the mixture on ice, extracting the filtered solution with ether and the washed ether solution with 180 cc. H2O containing 20 g. NaOH, and the acidified (36 cc. 50% H2SO4) solution again with ether give 16 g. oil, containing 80% HOCH2CF2CO2H (VI), turns dark and becomes more viscous when heated at 250°/8 mm. Refluxed 11 h. with 23 g. EtOH and 60 g. CuSO4, VI gives 7.9 g. HOCH2-CF2CO2Et (VII), b6 58-61°, b760 181°, nD25 1.3830. Hydrolysis of VII gives VI, m. 49-53°. Treating I at 30070 lb. and 60° 15 h. with 100 g. iodine in 150 cc. ether gives 74% (CF2I)2, b14 23°, b110 51°, b. 112-13°, nD25 1.4895, d425 2.6293, MR 40.3. N2O4 (57 g.) with I 8 h. at 7 lb. pressure gives 7.5% [CF2(NO2)]2, b. 58-9°, d425 1.6024, nD25 1.3265, MR 24.2.

ACCESSION NUMBER: 1950:29898 CAPLUS

L29 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

DOCUMENT NUMBER: 44:29898
ORIGINAL REFERENCE NO.: 44:5796f-i,5797a-e
TITLE: Addition reactions of tetrafluoroethylene
AUTHOR(S): Coffman, D. D.; Raasch, M. S.; Rigby, G. W.; Barrick, P. L.; Hanford, W. E.
CORPORATE SOURCE: E. I. Du Pont de Nemours & Co., Wilmington, DE
SOURCE: Journal of Organic Chemistry (1949), 14, 747-53
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 44:29898

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COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	29.43	486.41

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	-6.57	-114.61

STN INTERNATIONAL LOGOFF AT 17:22:32 ON 15 JUN 2005